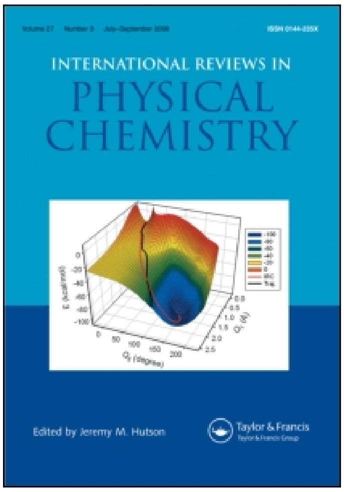

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Electronic spectra of carbon chains and derivatives

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Electronic spectra of carbon chains and derivatives

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Spectroscopic characterisation of carbon chains and ions has been motivated by a general interest in understanding the electronic structure and properties and also due to their prominence in astrochemistry, combustion processes as well as molecular electronics. Various experimental and theoretical approaches have been successfully implemented over the years towards realising this goal. In the current review, we have tabulated the experimentally available data on the excited electronic states of carbon chains and derivatives containing H, N, O, S and metals.

Keywords: carbon chains; heteroatom-doped carbon chains; ISM; diffuse interstellar bands

Contents

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1. Introduction

The first signs of molecules in the universe appeared during the recombination era, which marked the transition from an ionised state to a predominantly neutral environment made up of H, He, D and Li. Radiative association reactions triggered the formation of simple molecules, such as H_2, LiH and HD as well as molecular ions like He_2^+, HeH^+ and HD^+. As the universe began to cool and expand, stars were formed from giant clouds of hydrogen, thereby setting the stage for the formation of heavier and complex molecules containing C, O, N, S, P, halides and metals. Until now, approximately 150 molecules have been detected in the interstellar medium (ISM). From the first molecule CH to the most recent detection of ethylformate (C_2H_5OCHO) and *n*-propylcynide (C_3H_7CN) [1], it is clear that the interstellar chemistry is largely carbon dominated. These molecules are known to be confined to distinct environments like the circumstellar shells of carbon or oxygen rich stars, planetary nebula, diffuse and dense clouds [2,3]. Different formation mechanisms ranging from gas phase ion-molecule reactions and neutral–neutral collisions to adsorption–desorption processes on dust grains have been proposed [4,5]. The molecular composition of space and the reaction pathways leading to their formation remains an active area of research.

Molecules possess characteristic absorption/emission features generated by their electronic, vibrational and rotational motion; hence their detection in space and terrestrial environment relies on spectroscopy. Astronomical observations have been made possible by radio astronomy, infrared (IR) and optical telescopes. Over the years, laboratory experiments simulating the temperature, pressure and density conditions in space as well as computational tools have complemented the above observations.

Majority of the molecules detected in the interstellar and circumstellar medium are built up on a carbon–carbon framework. The ability of carbon to hybridise gives rise to an assortment of molecules ranging from the simplest C_2, to the longest conjugated system, $HC_{11}N$ and the larger and more stable polycyclic aromatic hydrocarbons. The list includes cations and anions as well. In this review, we focus on the experimentally available data on the electronic spectroscopy of carbon chains and their derivatives containing H, N, O, S and metals. An understanding of their electronic spectra allows one to make direct comparisons with astrophysical observations. Relevant in this context is the role of carbon chains which have been postulated as carriers of diffuse interstellar bands (DIBs): a group of nearly 200 absorption features in the 400–900 nm region with half widths ranging from

1 to 200 cm^{-1} [6,7]. Over the years, significant effort has been put forth in this direction by recording electronic spectra of mass selected carbon species in low-temperature matrices in conjunction with gas phase measurements [8,9]. Trends within a homologous series of carbon chains particularly with respect to the absorption wavelengths and oscillator strengths have emerged which have been instrumental in narrowing down the size and type molecule to be pursued as a potential DIB carrier. Until recently, the role of anions in the ISM was generally disregarded because efficient mechanisms for their formation were not known. Electron attachment to a polar neutral core via the dipole bound states (DBS) of anions (which are electronic states close to the detachment threshold) is now considered as a pathway to anion production in the ISM. Hydrogen terminated carbon chains, C_nH are known to have a high dipole moment and electron affinity; the corresponding C_4H^- [10], C_6H^- [11] and C_8H^- [12] were the first anions to be recently detected in space.

In the terrestrial environment, carbon chains play an important role in flame and soot chemistry [13]. Electron conducting properties which arise from conjugated π electron bonds in these chains (cumulenic or acetylenic structure) make them ideally suited for use as molecular wires in electronic systems [14,15]. From the perspective of fundamental research, it is interesting to study how the electronic structure, geometry and dynamics vary with the addition of different heteroatoms to bare carbon chains. An interesting example is the change in the ground state geometry from linear in the case of HC_nN systems to bent in HC_nO chains. Another feature is the alternation in molecular properties between even and odd members within a homologous series. For example, the ground state symmetry alternates between $^1\Sigma^+$ and $^3\Sigma^-$ in even–odd systems of the type C_nX (X = C, O, S), XC_nX (X = H, N, O, S) or HC_nX (X = N). This behaviour is also manifested in the binding energies, ionisation potentials and electron affinities leading to the preferential formation of certain chains.

In this review, we tabulate the ground and excited electronic state symmetries and band origins of carbon chains and derivatives recorded in the gas phase and in neon or other matrix environments. It must be emphasised that many of these molecules have also been investigated in detail via microwave [16] and IR spectroscopies [17] and have been the subject of numerous theoretical studies [18].

2. Bare carbon chains

2.1. C_n, C_n^+ and C_n^-

The structure and spectroscopic properties of bare carbon species and ions have been studied over the past several years. Calculations predict that linear cumulenic chains with $^1\Sigma_g^+$ ground electronic states are the low energy forms for the odd members while for the even-membered species C_4, C_6 and C_8, the linear structure ($^3\Sigma_g^-$) is nearly isoenergetic with the monocyclic ring isomer (^1A_g) [19,20]. Under experimental conditions, it is the linear form which appears to be entropically favoured and is readily formed in the gas phase and cryogenic matrices. Rotationally resolved infrared spectra are available for linear C_n up to $n = 13$ [21,22] in addition to the electronic spectra up to $n = 21$ (Table 1). Cyclic isomers of $C_6, C_8, \ldots, C_{14}$ have been trapped in Ar/Ne matrices [23–26] while the ring forms of C_{14}, C_{18} and C_{22} have been observed in the gas phase via a resonance enhanced multiphoton ionisation (REMPI) technique [27,28].

Table 1. Bare carbon chains: C_n species.

Species/electronic ground state	n	Origin (cm^{-1})	Phase	Reference
C_n	2	$A^1\Pi_u$ 8268	Gas	J. Mol. Spectrosc. **131**, 261 (1988)
n even X $^3\Sigma_g^-$		$D^1\Sigma_u^+$ 43,227		
($n=2$, X $^1\Sigma_g^+$)	3	$A^1\Pi_u$ 24,685	Gas	J. Chem. Phys. **122**, 244308 (2005)
n odd X $^1\Sigma_g^+$		$B^1\Delta_u$ 37,594–32,258	Ne matrix	J. Chem. Phys. **113**, 10999 (2000)
		$D^1\Delta_u$ 42,264		J. Chem. Phys. **125**, 244307 (2006)
		$^1\Sigma_u^+$ 62,500		J. Phys. Chem. A **106**, 5779 (2002)
	4	$^3\Sigma_u^-$ 26,323	Gas	J. Chem. Phys. **112**, 9777 (2000)
	5	$^1\Pi_u$ 19,599	Gas	J. Chem. Phys. **125**, 094308 (2006)
		$^1\Pi_u$ 22,470		
		$^1\Sigma_u^+$ 42,030		
	6	$1^3\Sigma_u^-$ 19,558	Ne matrix	J. Chem. Phys. **103**, 54 (1995)
		$2^3\Sigma_u^-$ 42,105	Gas	J. Chem. Phys. **125**, 094308 (2006)
	7	$^1\Pi_u$ 18,440	Ne matrix	J. Chem. Phys. **104**, 4954 (1996)
		$^1\Sigma_u^+$ 39,556		
	8	$1^3\Sigma_u^-$ 15,630	Ne matrix	J. Chem. Phys. **103**, 54 (1995)
		$2^3\Sigma_u^-$ 36,075	Gas	J. Chem. Phys. **125**, 094308 (2006)
	9	$^1\Sigma_u^+$ 34,700	Gas	J. Chem. Phys. **125**, 094308 (2006)
	10	$^3\Sigma_u^-$ 13,596	Ne matrix	J. Chem. Phys. **103**, 54 (1995)
	11	$^1\Sigma_u^+$ 29,732	Ne matrix	J. Chem. Phys. **104**, 4954 (1996)
	13	$^1\Sigma_u^+$ 26,341	Ne matrix	J. Chem. Phys. **104**, 4954 (1996)
	15	$^1\Sigma_u^+$ 23,832	Ne matrix	J. Chem. Phys. **104**, 4954 (1996)
	17	$^1\Sigma_u^+$ 21,719	Ne matrix	Chem. Phys. Lett. **304**, 35 (1999)
	19	$^1\Sigma_u^+$ 19,867	Ne matrix	Chem. Phys. Lett. **304**, 35 (1999)
	21	$^1\Sigma_u^+$ 18,387	Ne matrix	Chem. Phys. Lett. **304**, 35 (1999)
C_n^+	2	$B^4\Sigma_u^+$ 19,730	Gas	J. Chem. Phys. **88**, 4614 (1988)
n even X $^2\Pi_{g/u}$	6	$^2\Pi_g$ 15,484	Ne matrix	J. Chem. Phys. **120**, 7520 (2004)
($n=2$, X $^4\Sigma_g^+$)	7	A 12,985	Ne matrix	J. Chem. Phys. **123**, 044305 (2005)
n odd X $^2\Pi_{g/u}$		B 30,093		
		C 32,395		
	8	A 11,226	Ne matrix	J. Chem. Phys. **123**, 044305 (2005)
		B 16,624		
		C 16,729		
		D 19,268		
		E 32,453		
	9	A 26,918	Ne matrix	J. Chem. Phys. **123**, 044305 (2005)
C_n^-	2	$A^2\Pi_u$ 3928	Gas	J. Chem. Phys. **89**, 129 (1988)
n even X $^2\Pi_{g/u}$		$B^2\Sigma_u^+$ 18,483		Chem. Phys. Lett. **244**, 400 (1995)
($n=2$, X $^2\Sigma_g^+$)	3	$A^2\Delta_u$ 4743	Gas	J. Chem. Phys. **112**, 3747 (2000)
		$B^2\Sigma_u^-$ 25,948		
		$C^2\Sigma_u^+$ 28,507		
n odd X $^2\Pi_{g/u}$	4	$A^2\Sigma_g^+$ 8019	Ne matrix	J. Chem. Phys. **103**, 54 (1995)

(*continued*)

Table 1. Continued.

Species/electronic ground state	n	Origin (cm^{-1})	Phase	Reference
		$B^2\Sigma_u^+$ 10,789	Gas	Chem. Phys. **228**, 293 (1998)
		$C^2\Pi_u$ 21,896		
		$2^2\Pi_u$ 26,069		
		$3^2\Pi_u$ 29,036		
		$C^2\Pi_u$ 25,539		
		$2^2\Pi_u$ 25,989		
		$3^2\Pi_u$ 28,717		
C_n^-	5	$A^2\Pi_g$ 20,200	Ne matrix	J. Phys. Chem. A. **101**, 5292 (1997)
n even X $^2\Pi_{g/u}$		$B^2\Pi_g$ 27,847	Gas	Chem. Phys. **228**, 293 (1998)
n odd X $^2\Pi_{g/u}$		$A^2\Pi_g$ 20,164		
	6	$A^2\Sigma_g^+$9352	Ne matrix	J. Chem. Phys. **103**, 54 (1995)
		$C^2\Pi_u$ 16,453	Gas	J. Chem. Phys. **105**, 4905 (1996)
		$2^2\Pi_u$ 20,064		
		$3^2\Pi_u$ 22,517		
		$C^2\Pi_u$ 16,476		
	7	$A^2\Pi_g$ 15,954	Ne matrix	J. Phys. Chem. A. **101**, 5292 (1997)
		$B^2\Pi_g$ 20,314	Gas	Chem. Phys. **228**, 293 (1998)
		$C^2\Pi_g$ 35,231		
		$A^2\Pi_g$ 15,943		
		$B^2\Pi_g$ 20,298		
	8	$^2\Sigma_u^+$ 1047	Ne matrix	J. Chem. Phys. **107**, 4468 (1997)
		$C^2\Pi_u$ 12,933	Gas	J. Chem. Phys. **105**, 4905 (1996)
		$2^2\Pi_u$ 16,295		
		$C^2\Pi_u$ 12,963		
		$2^2\Pi_u$ 16,305		
	9	$A^2\Pi_g$ 13,082	Ne matrix	J. Phys. Chem. A. **101**, 5292 (1997)
		$B^2\Pi_g$ 16,468	Gas	Chem. Phys. **228**, 293 (1998)
		$C^2\Pi_g$ 29,446		
		$D^2\Pi_g$ 34,536		
		$A^2\Pi_g$ 13,080		
		$B^2\Pi_g$ 16,455		
		$C^2\Pi_g$ 29,334		
	10	$B^2\Sigma_g^+$8964	Ne matrix	J. Chem. Phys. **107**, 4468 (1997)
		$C^2\Pi_u$ 10,338	Gas	J. Chem. Phys. **109**, 1329 (1998)
		$2^2\Pi_u$ 13,596		
		$C^2\Pi_u$ 10380		
C_n^-	11	$A^2\Pi_g$ 11,042	Ne matrix	J. Phys. Chem. A. **101**, 5292 (1997)
n even X $^2\Pi_{g/u}$		$B^2\Pi_g$ 13,906	Gas	J. Chem. Phys. **106**, 9992 (1997)
n odd X $^2\Pi_{g/u}$		$C^2\Pi_g$ 25,151		
		$D^2\Pi_g$ 29,884		

(*continued*)

Table 1. Continued.

Species/electronic ground state	n	Origin (cm^{-1})	Phase	Reference
		A$^2\Pi_g$ 11,050		
	12	C$^2\Pi_u$ 8006	Ne matrix	J. Chem. Phys. **107**, 4468 (1997)
		2$^2\Pi_u$ 11,636	Gas	J. Phys. Chem. A. **104**, 8622 (2000)
		C$^2\Pi_u$ 8100		
	13	A$^2\Pi_g$ 9502	Ne matrix	Chem. Phys. Lett. **304**, 35 (1999)
		A$^2\Pi_g$ 9500	Gas	J. Chem. Phys. **106**, 9992 (1997)
		B$^2\Pi_g$ 11,300		
	14	C$^2\Pi_u$ 6849	Ne matrix	J. Chem. Phys. **107**, 4468 (1997)
		2$^2\Pi_u$ 10,202	Gas	J. Phys. Chem. A. **104**, 8622 (2000)
		C$^2\Pi_u$ 6900		
		2$^2\Pi_u$ 10,200		
	15	A$^2\Pi_g$ 8316	Ne matrix	Chem. Phys. Lett. **304**, 35 (1999)
		A$^2\Pi_g$ 8300	Gas	J. Phys. Chem. A. **104**, 8622 (2000)
		B$^2\Pi_g$ 10,100		
	16	C$^2\Pi_u$ 5784	Ne matrix	J. Chem. Phys. **103**, 54 (1995)
		C$^2\Pi_u$ 5800	Gas	J. Phys. Chem. A. **104**, 8622 (2000)
		2$^2\Pi_u$ 9100		
	17	A$^2\Pi_g$ 7382	Ne matrix	Chem. Phys. Lett. **304**, 35 (1999)
		A$^2\Pi_g$ 7300	Gas	J. Phys. Chem. A. **104**, 8622 (2000)
		B$^2\Pi_g$ 9100		
	18	C$^2\Pi_u$ 4833	Ne matrix	J. Chem. Phys. **103**, 54 (1995)
	19	A$^2\Pi_g$ 6612	Ne matrix	Chem. Phys. Lett. **304**, 35 (1999)
		A$^2\Pi_g$ 6600	Gas	J. Phys. Chem. A. **104**, 8622 (2000)
		B$^2\Pi_g$ 8200		
	20	C$^2\Pi_u$ 4099	Ne matrix	J. Chem. Phys. **103**, 54 (1995)
	21	A$^2\Pi_g$ 5974	Ne matrix	Chem. Phys. Lett. **304**, 35 (1999)
		A$^2\Pi_g$ 5900	Gas	J. Phys. Chem. A. **104**, 8622 (2000)
		B$^2\Pi_g$ 7500		
	22	C$^2\Pi_g$ 3449	Ne matrix	Chem. Phys. Lett. **304**, 35 (1999)

Structural information about carbon chain ions has been obtained by gas phase chromatography [29,30] and ion-molecule reactivity studies [31]. These suggest that species smaller than C_{10}^- exclusively exist as linear chains while both isomers coexist for systems from C_{10}^- to C_{30}^-. In the case of cations, ion-mobility studies indicate that for C_7^+–C_{10}^+ both the linear and ring structures coexist while only the latter is observed for larger species from C_{10}^+ to C_{20}^+.

Linear carbon chains have been characterised using a variety of experimental techniques and information about the excited electronic states, vibrational frequencies, electron affinities and ionisation potentials have been determined. Experimental data on the excited electronic states of bare carbon chains are presented in Table 1.

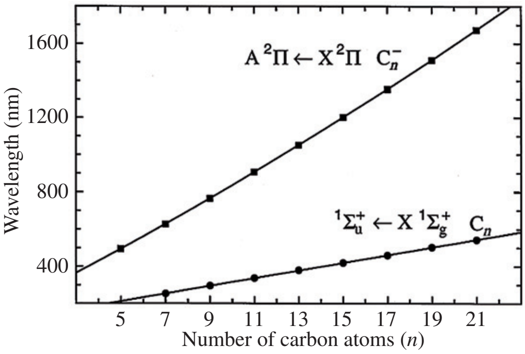

Figure 1. A plot of the origin band wavelength vs. the number of carbon atoms for the anionic and neutral odd-membered carbon chains.

The characteristic $\pi \leftarrow \pi$ electronic excitation in these systems results in the $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ (n even) and $^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ (n odd) transitions. These were measured by depositing mass selected carbon anions in 5 K neon matrices followed by electron detachment with a broad band UV source. Optical spectra corresponding to the above transitions were observed only up to C_{10} in the even chains and farther up to C_{21} in the odd chains consistent with the other experimental observations which demonstrate a change in geometrical structure above C_{10}.

The matrix measurements have been the basis for gas phase studies of carbon chains. C_2 and C_3 are the best characterised of these. They have been detected in diffuse and translucent molecular clouds via their electronic transitions [32,33]. In addition, C_3 and C_5 have been detected in circumstellar shells of the carbon rich star, IRC+10216 by IR spectroscopy [34]. Consequently, a gas phase study of C_4 was undertaken and a partly rotationally resolved spectrum of the origin band of the $^3\Sigma_u^- \leftarrow X\,^3\Sigma_g^-$ transition was recorded using the cavity ring down (CRD) technique. Electronic spectra of C_5, C_6, C_8 and C_9 have been measured in the gas phase by REMPI spectroscopy. Figure 1 shows a plot of the origin band wavelength versus the number of carbon atoms for the $^1\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ and the A $^2\Pi \leftarrow X\,^2\Pi$ band system of the neutral and anionic odd-membered carbon chains. The band origin shifts to the red with increasing chain length. In the case of C_5, three excited states were observed in which the spectral features were significantly broad and could not be rotationally resolved. This has been attributed to fast intramolecular processes occurring on a picosecond to femtosecond time scale. The intramolecular dynamics are depicted in Figure 2; upon electronic excitation, the molecule can either relax to higher vibrational levels of the ground state or get trapped in a nearby long-lived triplet state from where it can be subsequently ionised. The predissociative nature of the 2 $^3\Sigma_u^-$ excited state of C_6 and C_8 and $^1\Sigma_u^+$ of C_9 was confirmed by a dissociative 'hole burning' approach in which a decrease in the ion current due to predissociation of the species of interest is monitored.

Carbon chain anions are open shell systems with $^2\Pi_{g/u}$ ground states. The neutrals, C_n ($n = 2$–11) have high electron affinities, in the range of 2.8–4.4 eV [35], resulting in one or more bound excited electronic states below the photodetachment threshold. C_3^- with an electron affinity of 1.99 eV is the only anion, which does not possess a bound excited state.

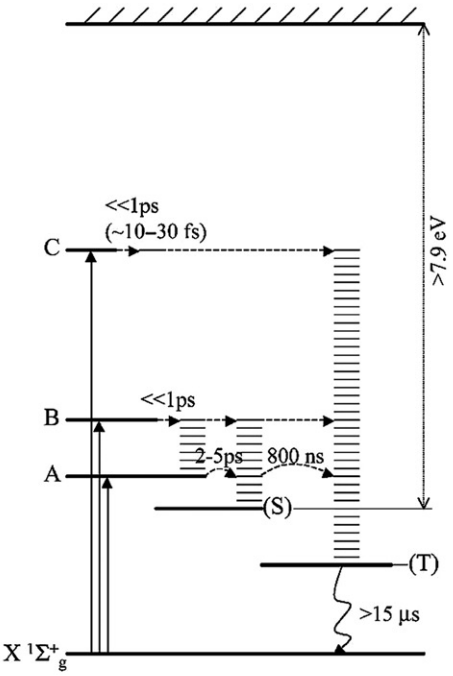

Figure 2. Inferred intramolecuar dynamics in excited electronic states of C_5.

UV-Vis absorption spectra of mass selected anions, C_{2n+1}^- ($n = 2$–10) and C_{2n}^- ($n = 2$–11) were first observed in rare gas matrices. Several electronic transitions were identified and assigned as $^2\Pi \leftarrow X\ ^2\Pi$ excitation. In addition, the $^2\Sigma^+ \leftarrow X\ ^2\Pi$ transitions have been observed for C_{2n}^- ($n = 2$–5). Electronic spectra of anions in the gas phase have been measured using one- or two-colour resonant photodetachment technique. Excited states lying above the electron detachment threshold referred to as Feshbach states have been observed for C_3^- and C_5^-. Results from the matrix studies were used to assign several $^2\Pi \leftarrow X\ ^2\Pi$ transitions of the corresponding even and odd chains listed in Table 1.

In contrast to the neutral and anionic chains, experimental data on the electronic spectra of the cationic chains is limited. The B $^4\Sigma_u^+ \leftarrow X\ ^4\Sigma_g^+$ band system of C_2^+ was observed in the gas phase and rotationally resolved by laser excitation spectroscopy. Recently, the $^2\Pi_g \leftarrow X\ ^2\Pi_g$ transition of C_6^+ and several dipole allowed transitions of linear C_7^+, C_8^+ and C_9^+ have been observed in neon matrices along with their cyclic counterparts.

3. Hydrogen terminated carbon chains

3.1. C_nH, C_nH^+ and C_nH^-

Hydrogen terminated carbon chain radicals, C_nH ($n = 2$–8) have been detected in dark molecular clouds and envelopes of evolved stars [36]. The ground electronic states have been well characterised for C_nH ($n = 2$–11) by microwave spectroscopy [37]. The dominant ground state electronic configuration for the even chains with $n = 2$, 4 is $\pi^4\sigma^1$ giving $^2\Sigma^+$

symmetry; for $n \geq 6$ it is $\sigma^2\pi^3$ yielding a $^2\Pi_i$ ground state. In the odd chains, the π highest occupied molecular orbital (HOMO) is singly occupied with $\sigma^2\pi^1$ configuration resulting in a $^2\Pi_r$ ground electronic state. These are known to exist in both cyclic and linear forms, with the latter becoming more stable with increasing n. For example, in C_3H, C_5H and C_7H, the energy difference between the linear and cyclic isomers increases by 7.5, 15.5 and 21.3 kJ mol^{-1}, respectively [38–40].

In the odd members, the lowest electronic states arise from $\pi \leftarrow \sigma$ excitation giving $^4\Sigma^-$, $^2\Delta$, $^2\Sigma^+$ and $^2\Sigma^-$ excited states while $\pi \leftarrow \pi$ electron promotion results in excited states with $^2\Phi$, $^4\Pi$ and $^2\Pi(3)$ symmetries. The dipole allowed states include $^2\Delta$, $^2\Sigma^+$, $^2\Sigma^-$ and $^2\Pi(3)$. Optical spectra have been recorded for C_nH ($n = 3$, 5, 7 and 9) by a REMPI technique. In the case of C_3H, a complex vibronic spectrum with a Franck-Condon profile showing a large change in geometry was observed and in conjunction with *ab initio* calculations the spectral features were assigned to linear–bent excitations. Three trans-bent excited states were observed with A^2A' and B^2A'' correlating to $^2\Delta$ in the linear configuration and a C^2A'' state higher in energy. Unlike C_3H, the electronic spectra of the longer chains did not show a large geometry change and were assigned to linear–linear excitations. The band origins for the observed dipole allowed transitions are listed in Table 2, Panel A. The lowest excited states, A $^2\Delta$ and B $^2\Sigma^+$ for C_9H were not observed in the REMPI spectrum, which was recorded using 7.9 eV photons as the ionisation source; ionisation potential of C_9H is expected to be greater than 10.2 eV. However, transitions to these states are predicted to lie around 660 and 595 nm, respectively.

In the even numbered chains, the electronic spectra show signatures of vibronic coupling between the low-lying $^2\Sigma^+$ and $^2\Pi$ states. The $^2\Pi$ state progressively becomes lower in energy as the chain length increases. The energy spacing between the two states has been deduced from the photoelectron spectra of the corresponding anions. In C_2H and C_4H, the $^2\Pi$–$^2\Sigma^+$ spacing is around 0.46 and 0.06 eV while the $^2\Sigma^+$–$^2\Pi$ separation for C_6H and C_8H is around 0.18 and 0.25 eV, respectively [41]. The second excited state, $B^2\Pi$ has been observed in the gas phase for chains up to $n = 10$ and in neon matrices up to $n = 16$.

The even chain anions are closed shell species with $^1\Sigma^+$ (π^4) ground electronic state, while the odd members exhibit $^3\Sigma^-$ (π^2) symmetry. $\pi \leftarrow \pi$ excitation in both systems gives rise to $^{1,3}\Sigma^+$, $^{1,3}\Sigma^-$ and $^{1,3}\Delta$ excited states. Electronic absorption spectra of the dipole allowed $^1\Sigma^+ \leftarrow X\,^1\Sigma^+$ transition in the even series, C_nH^- ($n = 10, 12, \ldots, 24$) and $^3\Sigma^- \leftarrow X^3\Sigma^-$ in the odd series, C_nH^- ($n = 9$–15) have been observed; the spectral features assigned to two isomers. The first being the more stable linear acetylenic chain while the second a bent cumulene-like isomer with a quasilinear carbon chain framework and an off axis terminal hydrogen atom. For the second isomer, the bands were assigned to a $^1A' \leftarrow X\,^1A'$ transition.

Excited electronic states close to the electron detachment threshold have been observed for the smaller anions, C_3H^-, C_4H^-, C_6H^- and C_8H^-. These are the DBS where the electron is weakly bound to the dipole field of the neutral [42]. A high electron affinity and dipole moment (>2D) of the corresponding neutral are considered as prerequisites for their formation. Electronic transitions to the DBS of the above anions were observed by resonance enhanced multiphoton dissociation spectroscopy and assigned to $^1\Pi \leftarrow X\,^1\Sigma^+$ of C_6H^- and C_8H^-, and $^1A'(^1\Pi) \leftarrow X\,^1\Sigma^+$ of C_4H^-. In C_6H^- and C_8H^-, the DBS arise from the X $^2\Pi$ configuration of the neutrals which have dipole moments of 4.79 and 5.26 D [43], respectively. In the case of C_4H^-, the 0.8 D dipole moment of X $^2\Sigma^+$ [44] is too low to

Table 2. H terminated carbon chains.

Species/electronic ground state	*n*	Origin (cm^{-1})	Phase	Reference
Panel A: C_nH species				
C_nH	2	$A^2\Pi$ 3750	Gas	J. Chem. Phys. **108**, 10018 (1998)
		$B^2\Sigma^+$ 24,033		
n even X $^2\Sigma^+$ ($n=2,4$)				J. Mol. Spectrosc. **217**, 249 (2003)
X $^2\Pi_i$ ($n \geq 6$)	3	A^2A' 19,187	Gas	J. Chem. Phys. **115**, 6913 (2001)
		B^2A'' 20,538		
		C^2A'' 23,171		
n odd X $^2\Pi_r$	4	$A^2\Pi$ 468	Gas	J. Chem. Phys. **108**, 10018 (1998)
		$B^2\Sigma^+$ 24,033		J. Chem. Phys. **108**, 3465 (1998)
	5	$A^2\Delta$ 18,791	Gas	J. Chem. Phys. **117**, 8362 (2002)
		$B^2\Sigma^-$ 20,608		
	6	$A^2\Sigma^+$ 1460	Gas	J. Chem. Phys. **108**, 10018 (1998)
		$B^2\Pi$ 18,990		Faraday Diss. **109**, 109 (1998)
	7	$A^2\Delta$ 16,819	Gas	J. Chem. Phys. **117**, 8362 (2002)
		$B^2\Sigma^-$ 18,532		
		$C^2\Sigma^+$ 20,627		
	8	$A^2\Sigma^+$ 2041	Gas	J. Chem. Phys. **108**, 10018 (1998)
		$B^2\Pi$ 15,973		Chem. Phys. Lett. **382**, 245 (2003)
	9	$C^2\Sigma^+$ 18,799	Gas	J. Chem. Phys. **117**, 8362 (2002)
		$D^2\Pi$ 20,205		
		$F^2\Pi$ 23,509		
	10	$B^2\Pi$ 14,003	Gas	J. Chem. Phys. **109**, 3819 (1998)
	12	$B^2\Pi$ 12,492	Ne matrix	J. Chem. Phys. **103**, 54 (1995)
	14	$B^2\Pi$ 11,554	Ne matrix	J. Chem. Phys. **103**, 54 (1995)
	16	$B^2\Pi$ 10,821	Ne matrix	J. Chem. Phys. **103**, 54 (1995)
C_nH^+	6	$^3\Sigma^-$ 15,913	Ne matrix	J. Phys. Chem. A. **110**, 2885 (2006)
n even X $^3\Sigma^-$	8	$^3\Sigma^-$ 19,387	Ne matrix	J. Phys. Chem. A. **110**, 2885 (2006)
C_nH^-	3	$d^3A'' \leftarrow a^3A''$	Gas	Mol. Phys. **102**, 1881 (2004)
n even X $^1\Sigma^+$				
		18,042		
n odd X $^3\Sigma^-$	4	$^1A'$ ($^1\Pi$) 28,710	Gas	J. Chem. Phys. **108**, 10018 (1998)
Acetylenic isomer (a)		$^1A'$ ($^1\Pi$) 28,643		Mol. Phys. **101**, 583 (2003)
$^3\Sigma^- \leftarrow$ X $^3\Sigma^-$	6	$^1\Pi$ 30,408	Gas	J. Chem. Phys. **116**, 6126 (2002)
$^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$	8	$^1\Sigma^+$ 35,174	Ne matrix	J. Chem. Phys. **110**, 1492 (1999)
Cumulenic isomer (c)		$^1\Pi$ 31,497	Gas	J. Chem. Phys. **116,** 6126 (2002)
$A' \leftarrow X^1A'$	9	$^3\Sigma^-$ 27,630 (a)	Gas	J. Phys. Chem. A. **103**, 9712 (1999)
		^1A 29,014 (c)		
	10	$^1\Sigma^+$ 30,479 (a)	Gas	J. Chem. Phys. **111**, 9280 (1999)

(*continued*)

Table 2. Continued.

Species/electronic ground state	n	Origin (cm^{-1})	Phase	Reference
		$^1A'$ 27,847 (c)	Ne matrix	
	11	$^3\Sigma^-$ 24,288 (a)	Gas	J. Phys. Chem. A. **103**, 9712 (1999)
		$^1A'$ 26,742 (c)		
	12	$^1\Sigma^+$ 26,802 (a)	Gas	J. Chem. Phys. **111**, 9280 (1999)
		$^1A'$ 25,654 (c)	Ne matrix	
	13	$^3\Sigma^-$ 24,288 (a)	Gas	J. Phys. Chem. A. **103**, 9712 (1999)
		$^1A'$ 26,742 (c)		
	14	23,837 (a + c)	Ne matrix	J. Chem. Phys. **111**, 9280 (1999)
		23,763 (a + c)	Gas	
	15	$^3\Sigma^-$ 19,434 (a)	Gas	J. Phys. Chem. A. **103**, 9712 (1999)
		$^1A'$ 23,284 (c)		
	16	$^1\Sigma^+$ 21,226 (a)	Gas	J. Chem. Phys. **111**, 9280 (1999)
		$^1A'$ 21,852 (c)	Ne matrix	
	18	$^1\Sigma^+$ 19,226 (a)	Gas	J. Chem. Phys. **111**, 9280 (1999)
		$^1A'$ 20,152 (c)	Ne matrix	
	20	$^1\Sigma^+$ 17,592 (a)	Gas	J. Chem. Phys. **111**, 9280 (1999)
		$^1A'$ 18,641 (c)	Ne matrix	
	22	$^1A'$ 17,647 (c)	Ne matrix	J. Chem. Phys. **111**, 9280 (1999)
	24	$^1A'$ 16,731 (c)	Ne matrix	J. Chem. Phys. **111**, 9280 (1999)
Panel B: HC$_n$H species				
HC$_n$H	2	$B^1\Sigma_u^+$74,962	Gas	Helv. Chim. Acta. **57**, 1731 (1974)
n even X $^1\Sigma_g^+$	4	$B^1\Sigma_u^+$60,864	Gas	Helv. Chim. Acta. **57**, 1731 (1974)
n odd X $^3\Sigma_g^-$	6	$B^1\Sigma_u^+$54,615	Gas	Helv. Chim. Acta. **57**, 1731 (1974)
		$A^1\Delta_u$ 34,091		Phys. Chem. Chem. Phys. **5**, 4772 (2003)
	8	$B^1\Sigma_u^+$48,239	Gas	Helv. Chim. Acta. **57**, 1731 (1974)
		$A^1\Delta_u$ 29,454		Phys. Chem. Chem. Phys. **5**, 4772 (2003)
	10	$B^1\Sigma_u^+$ 43,784	Gas	J. Phys. Chem. A. **113**, 11099 (2009)
		$A^1\Delta_u$ 26,894		Phys. Chem. Chem. Phys. **5**, 4772 (2003)
	12	$B^1\Sigma_u^+$40,371	Gas	J. Phys. Chem. A. **113**, 11099 (2009)
		$A^1\Delta_u$ 25,046		Phys. Chem. Chem. Phys. **5**, 4772 (2003)
	14	$B^1\Sigma_u^+$37,667	Gas	J. Phys. Chem. A. **113**, 11099 (2009)
		$A^1\Delta_u$ 23,501		Phys. Chem. Chem. Phys. **5**, 4772 (2003)
	16	$B^1\Sigma_u^+$35,541	Gas	J. Chem. Phys. **114**, 2208 (2001)
	18	$B^1\Sigma_u^+$33,784	Gas	J. Chem. Phys. **114**, 2208 (2001)
	20	$B^1\Sigma_u^+$32,378	Gas	J. Chem. Phys. **114**, 2208 (2001)
	22	$B^1\Sigma_u^+$31,184	Gas	J. Chem. Phys. **114**, 2208 (2001)
	24	$B^1\Sigma_u^+$30,193	Gas	J. Chem. Phys. **114**, 2208 (2001)
	26	$B^1\Sigma_u^+$29,368	Gas	J. Chem. Phys. **114**, 2208 (2001)
n odd: $^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$	3	C_3H_2 X^1A_1	Gas	J. Mol. Spectrosc. **237**, 70 (2006)

(*continued*)

Table 2. Continued.

Species/electronic ground state	n	Origin (cm^{-1})	Phase	Reference
		A 13885–16389		
		B 16161–24802		
		C 39051–47156		
	5	$A^3\Sigma_u^-$ 23,033	Ne matrix	J. Chem. Phys. **103**, 8805 (1995)
	7	$A^3\Sigma_u^-$ 19,818	Gas	J. Chem. Phys. **119**, 814 (2003)
	9	$A^3\Sigma_u^-$ 17,185	Gas	J. Chem. Phys. **119**, 814 (2003)
	11	$A^3\Sigma_u^-$ 15,293	Gas	J. Chem. Phys. **119**, 814 (2003)
	13	$A^3\Sigma_u^-$ 13,916	Gas	J. Chem. Phys. **119**, 814 (2003)
		$B^3\Sigma_u^-$ 35,473		
	19	$B^3\Sigma_u^-$ 29,481	Gas	J. Chem. Phys. **119**, 814 (2003)
HC_nH^+	2	A^2A 39,109	Gas	Chem. Phys. Lett. **174**, 109 (1990)
n even X $^2\Pi$		$B^2\Sigma^+$ 56,380		
n odd X $^2\Pi$		$C^2\Sigma^+$ 92,460		
	4	$A^2\Pi$ 19,722	Gas	Can. J. Phys. **34**, 1046 (1956)
		$A^2\Pi$ 19,645	Ne matrix	Chem. Phys. **189**, 335 (1994)
		$C^2\Pi$ 29,753		J. Phys. Chem. **111**, 1831 (2007)
	5	$A^2\Pi$ 20,026	Ne matrix	Chem. Phys. **189**, 335 (1994)
	6	$A^2\Pi$ 16,654	Gas	J. Chem. Phys. **89**, 6081 (1988)
		$A^2\Pi$ 16,535	Ne matrix	Chem. Phys. **189**, 335 (1994)
		$C^2\Pi$ 23,939		J. Phys. Chem. **111**, 1831 (2007)
	7	$A^2\Pi$ 16,676	Ne matrix	Chem. Phys. **189**, 335 (1994)
	8	$A^2\Pi$ 14,143	Gas	J. Chem. Phys. **110**, 296 (1999)
		$A^2\Pi$ 14,017	Ne matrix	Chem. Phys. **189**, 335 (1994)
		$B^2\Pi$ 17,590		J. Phys. Chem. **111**, 1831 (2007)
		$C^2\Pi$ 20,194		
		$E^2\Pi$ 41,254		
	9	$A^2\Pi$ 14,387	Ne matrix	Chem. Phys. **189**, 335 (1994)
	10	$A^2\Pi$ 12,260	Gas	Chem. Phys. Lett. **313**, 171 (1999)
		$A^2\Pi$ 12,143	Ne matrix	Chem. Phys. **189**, 335 (1994)
		$B^2\Pi$ 15,404		J. Phys. Chem. **111**, 1831 (2007)
		$C^2\Pi$ 17,627		
		$E^2\Pi$ 36,284		
	11	$A^2\Pi$ 12,674	Ne matrix	Chem. Phys. **189**, 335 (1994)
	12	$A^2\Pi$ 10,703	Ne matrix	Chem. Phys. **189**, 335 (1994)
		$B^2\Pi$ 13,708		J. Phys. Chem. **111**, 1831 (2007)
		$D^2\Pi$ 18,570		
		$E^2\Pi$ 32,382		
	13	$A^2\Pi$ 11,418	Ne matrix	Chem. Phys. **189**, 335 (1994)
	14	$A^2\Pi$ 9548	Ne matrix	Chem. Phys. **189**, 335 (1994)
		$B^2\Pi$ 12,447		J. Phys. Chem, 2007, 111, 1831
		$D^2\Pi$ 16,399		
		$E^2\Pi$ 31,095		
	15	$A^2\Pi$ 10,422	Ne matrix	Chem. Phys. **189**, 335 (1994)
	16	$A^2\Pi$ 8620	Ne matrix	Chem. Phys. **189**, 335 (1994)

(*continued*)

Table 2. Continued.

Species/electronic ground state	n	Origin (cm^{-1})	Phase	Reference
HC_nH^-	12	$^2\Pi$ 12,814	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
$^2\Pi$ (1,2,3) $\leftarrow$ X $^2\Pi$		$^2\Pi$ 13,990		
		$^2\Pi$ 31,506		
	14	$^2\Pi$ 11,633	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 12,900		
		$^2\Pi$ 29,070		
	16	$^2\Pi$ 10,540	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 12,522		
		$^2\Pi$ 26,940		
	18	$^2\Pi$ 9626	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 10,506		
		$^2\Pi$ 27,248		
	20	$^2\Pi$ 8809	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 9887		
		$^2\Pi$ 23,635		
	22	$^2\Pi$ 8139	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 9393		
		$^2\Pi$ 22,282		
	24	$^2\Pi$ 7545	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 21,218		
Odd n	3	A^2A_1 14,294	Gas	J. Chem. Phys. **105**, 10696 (1996)
$C_3H_2^-$ X^2B_1		B^2A'' 18,244		Phys. Chem. Chem. Phys. **3**, 4674 (2001)
		C^2A_1 20,055		
		D^2B_1 27,754		

support a DBS; instead it arises from the low-lying A $^2\Pi$ state which is known to have a dipole moment around 4–5 D [45].

For the cationic species, electronic absorption spectra have been observed only for C_6H^+ and C_8H^+. These have $^3\Sigma^-$ ground states and are isoelectronic with the corresponding neutral carbon chains. The electronic spectra have been assigned to the linear $^3\Sigma^- \leftarrow X\ ^3\Sigma^-$ transition and are found to lie in the vicinity of the corresponding transitions in C_6 and C_8. In the case of C_8H^+ additional weak transitions towards the UV have been observed as well.

3.2. HC_nH, HC_nH^+ and HC_nH^-

The even-membered neutral polyacetylenes are closed shell species with $^1\Sigma_g^+$ (π_g^4/π_u^4) ground state like the corresponding isoelectronic C_nH^- chains. The smaller members, HC_4H and HC_6H have been detected in the ISM [46–48]. $\pi \leftarrow \pi$ excitation in these systems gives rise to the lowest excited states of $^{1,3}\Sigma_u^+$, $^{1,3}\Sigma_u^-$ and $^{1,3}\Delta_u$ symmetry. The intense dipole allowed B $^1\Sigma^+ \leftarrow X\ ^1\Sigma^+$ transition has been observed in the gas phase for

$n = 2, 4, \ldots, 26$, in neon matrices for $n = 12, 14, \ldots, 24$ and in solution for $n = 10, 12, \ldots, 20$–24. The REMPI spectra of the above band system for $n = 16$–26 are displayed in Figure 3. The bands lie in the UV and are dominated by progressions in the acetylenic stretching mode in the excited state; the frequency decreasing with the chain size. The transitions also exhibit intrinsic lifetime broadening which has been attributed to fast intramolecular relaxation processes. Density functional theory (DFT) calculations predict a significant single–triple bond length alternation in the ground state indicating an acetylenic structure [49]. This is expected to be less pronounced in the excited state resulting in a cumulene-like structure. The dipole forbidden transitions to the $^1\Delta_u$ and $^1\Sigma_u^-$ states become allowed in the even chains via Herzberg–Teller vibronic coupling. These have been observed for $n = 4$–14 by REMPI.

The odd-membered polyacetylenes are open shell species with $^3\Sigma_g^-$ ground states arising from $\pi_g^4\ \pi_u^2/\pi_u^4\pi_g^4$ electronic configuration. $\pi \leftarrow \pi$ excitation from a fully occupied inner orbital to the HOMO and that from HOMO to lowest unoccupied molecular orbital (LUMO) gives two triplet excited states designated as A $^3\Sigma_u^-$ and B $^3\Sigma_u^-$. The A $^3\Sigma_u^- \leftarrow \text{X}\ ^3\Sigma_g^-$ transition which lies in the visible has been observed for HC_nH, $n = 5, 7, \ldots, 15$ in neon matrices and for $n = 7$, 9, 11 and 13 in the gas phase. Calculations predict that the more intense B $^3\Sigma_u^- \leftarrow \text{X}\ ^3\Sigma_g^-$ transition begins in the VUV for HC_5H (170 nm) [50] and extends into the UV for HC_9H (210 nm) [51]. The B $^3\Sigma_u^-$ state

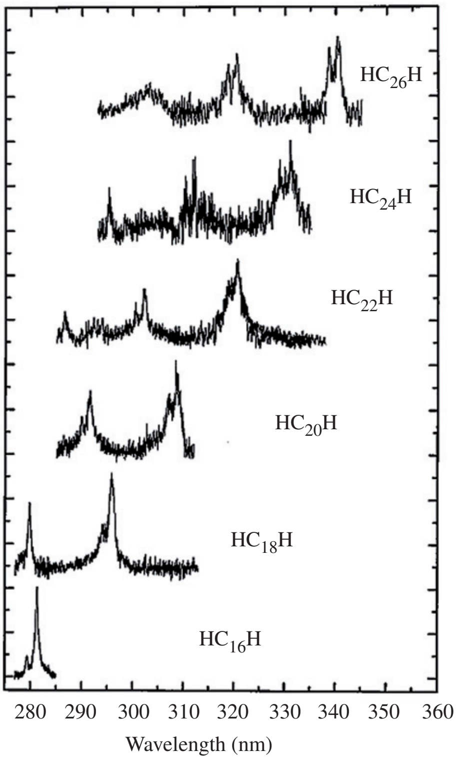

Figure 3. Resonant two-colour, two-photon ionisation spectra of the $^1\Sigma_u^+ \leftarrow \text{X}\ ^1\Sigma_g^+$ transition of polyynes $HC_{2n}H$ ($n = 8$–13).

has been observed for $HC_{13}H$ (280 nm) and $HC_{19}H$ (340 nm) by REMPI. Oscillator strengths (*f*) for the two transitions for $n = 5,7,\ldots,19$ were calculated at the CASSCF level of theory [52]. The *f*-value of the $A \leftarrow X$ transition appears to first increase up to $n = 7$ and then decrease with the chain size while for the $B \leftarrow X$ transition *f* gradually increases, converging at higher *n*. This behaviour has been explained in terms of configuration mixing between the A and B states, beginning with nearly equal contribution from the two for smaller chains and gradually taken over by the B state for larger systems.

The even/odd numbered polyacetylene cations have $^2\Pi$ ground states arising from π^3/π^1 configuration. Electronic absorption spectra of the (A, B, C, D and E) $^2\Pi \leftarrow X\ ^2\Pi$ transitions have been observed in neon matrices for $n = 2,4,\ldots,16$. The $A^2\Pi \leftarrow X\ ^2\Pi$ systems have also been studied in the gas phase for $n = 2$, 4 by laser induced fluorescence (LIF), $n = 6$, 8 and 10 by CRDS and $n = 4$, 6 and 8 in a radio frequency trap by two-colour excitation–dissociation approach. For the odd chains $n = 5,7,\ldots,15$ another set of matrix absorptions have been tentatively assigned to the $A^2\Pi \leftarrow X\ ^2\Pi$ transition. Like the cations, the polyacetylene anions have $^2\Pi$ ground states as well. Three excited electronic states, all assigned to $^2\Pi$ symmetry have been observed in 6 K neon matrices for even chains, $n = 12,14,\ldots,24$. The first two $^2\Pi \leftarrow X\ ^2\Pi$ transitions overlap in the IR and show progressions in the acetylenic stretching mode while the third $^2\Pi \leftarrow X\ ^2\Pi$ transition lies in the UV. In the odd chains, linear $C_3H_2^-$ isomer has been investigated by resonant two-photon detachment spectroscopy. The lowest excited state is a DBS while three higher excited states above the photodetachment threshold characterised as Feshbach states were observed.

4. Nitrogen and phosphorous terminated carbon chains

4.1. C_nN, C_nN^+ and C_nN^-

Among the radicals of the type C_nN, the odd-membered species CN, C_3N and C_5N have been detected in the ISM [53,54]. These have been shown to have a $^2\Sigma^+$ ground state arising from a $\pi^4\sigma^1$ configuration. The higher members $n \geq 9$ exhibit a $^2\Pi$ ground state with a $\pi^4\pi^1$ configuration similar to the even-membered chains [55,56]. As evident from Table 3, Panel A, experimental information on the excited electronic states of the even chains is sparse with the exception of C_2N whose absorption spectrum was obtained in the flash photolysis of diazoacetonitrile. Recently, the LIF spectrum of the $B\ ^2\Pi \leftarrow X\ ^2\Sigma^+$ band system of C_3N was measured and a Renner–Teller (RT) analysis of the B state was presented. Rotational analysis confirmed $^2\Pi_{3/2}$ as the lower component indicating that the excited state is inverted with a π^3 configuration. Figure 4 depicts the rotationally resolved LIF spectrum of the $B\ ^2\Pi_{3/2} \leftarrow X\ ^2\Sigma^+$ component of the origin band. The $C_{2n-1}N$ chains are isoelectronic with the $C_{2n}H$ species and like the latter have two low-lying $^2\Sigma^+$ and $^2\Pi$ states. In the case of C_3N, dispersed fluorescence measurements from the B state have shown that the $X\ ^2\Sigma^+ - A\ ^2\Pi$ spacing is around 1840 cm^{-1}. Theoretical studies indicate that the energy difference between these states decreases with the chain length leading to a change in the ground state symmetry from $^2\Sigma^+$ to $^2\Pi$ at C_7N [55]. Electronic absorption spectra of the longer chains $C_{2n-1}N$ ($n = 3$–7) have been recorded in 6 K neon matrices. These have been assigned to $B\ ^2\Pi \leftarrow X\ ^2\Pi$ for $n = 5$–7 and $B\ ^2\Pi \leftarrow X\ ^2\Sigma^+$ for $n = 3$ and 4. Based on the similarities in the spectral profile and vibrational pattern, it has been proposed that C_7N like C_5N has a $^2\Sigma^+$ ground state.

Table 3. N terminated carbon chains.

Species/electronic ground state	*n*	Origin (cm^{-1})	Phase	Reference
Panel A: C_nN species	2	**CCN isomer**		
C_nN		$A^2\Delta$ 21,2534	Ne matrix	Helv. Chim. Acta. **84**, 1432 (2001)
n even $X\ ^2\Pi$		$B^2\Sigma^-$ 22,437		
n odd $X\ ^2\Sigma^+$		$C^2\Sigma^+$ 26,652		
		D 27,330		
		A 21,259	Gas	Can. J. Phys. **44**, 353 (1996)
		B 22,413		
		C 26,662		
		CNC isomer		
		$A^2\Delta_u$ 30,303	Ne matrix	Helv. Chim. Acta. **84**, 1432 (2001)
		$B^2\Sigma_u^-$34,662		
		A 30,338	Gas	Can. J. Phys. **44**, 353 (1996)
		B 34,802		
	3	$A^2\Pi$ 1844	Gas	J. Chem. Phys. **127**, 184304 (2007)
		$B^2\Pi$ 27,929		
	5	$B^2\Pi$ 21,259	Ne matrix	J. Chem. Phys. **110**, 1492 (1999)
	7	$B^2\Pi$ 17,185	Ne matrix	J. Chem. Phys. **110**, 1492 (1999)
	9	$B^2\Pi$ 14,802	Ne matrix	J. Chem. Phys. **110**, 1492 (1999)
	11	$B^2\Pi$ 13,207	Ne matrix	J. Chem. Phys. **110**, 1492 (1999)
	13	$B^2\Pi$ 12,085	Ne matrix	J. Chem. Phys. **110**, 1492 (1999)
C_nN A $^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$	7	$A^1\Sigma^+$ 36,496	Ne matrix	J. Chem. Phys. **110**, 1492 (1999)
	9	$A^1\Sigma^+$ 30,656	Ne matrix	J. Chem. Phys. **110**, 1492 (1999)
n even $X\ ^3\Sigma^-$	11	A $^1\Sigma^+$ 26,295	Ne matrix	J. Chem. Phys. **110**, 1492 (1999)
n odd $X\ ^1\Sigma^+$	13	A $^1\Sigma^+$ 22,619	Ne matrix	J. Chem. Phys. **110**, 1492 (1999)
C_nN^+ $A^1\Pi \leftarrow X\ ^1\Sigma^+$	2	CCN^+ 21,637	Ne matrix	Helv. Chim. Acta. **84**, 1432 (2001)
		CNC^+ 30,703		

Panel B: NC$_n$N species				
NC$_n$N	2	$^1\Sigma_u^+$ 75,757	UV absorption	J. Mol. Spectrosc. **30**, 162 (1969)
n even X $^1\Sigma_g^+$		$^1\Pi_u$ 60,422		J. Mol. Spectrosc. **41**, 20 (1972)
n odd X $^3\Sigma_g^-$		$^1\Delta_u$ 48,309		J. Mol. Spectrosc. **39**, 393 (1971)
		$^1\Sigma_u^+$ 45,454		Proc. Phys. Soc. Lond. **82**, 335 (1963)
		$^3\Delta_u$ 40,000		
		$^3\Sigma_u^-$ 33,333		
	3	A 27,850	Ar matrix	Spectrochim. Acta. **50A**, 209 (1994)
		B 37,310		
	4	$^1\Delta_u$ 37,313	UV absorption	Spectrochim Acta. **12**, 521 (1958)
		$^1\Sigma_u^-$ 35,714		
	5	$^3\Sigma_u^-$ 22,836	Ne matrix	Chem. Phys. Lett. **351**, 85 (2002)
		$^3\Sigma_u^-$ 22,763	Gas	Chem. Phys. Lett. **345**, 89 (2001)
	6	$^1\Sigma_u^+$ 32,258	UV absorption	J. Chem. Phys. **52**, 5184 (1970)
	8	$^1\Sigma_u^+$ 43,103	Solution	Chem. Eur. J. **3**, 1105 (1997)
	10	$^1\Sigma_u^+$ 38,610	Solution	Chem. Eur. J. **3**, 1105 (1997)
	12	$^1\Sigma_u^+$ 35,460	Solution	Chem. Eur. J. **3**, 1105 (1997)
	14	$^1\Sigma_u^+$ 33,003	Solution	Chem. Eur. J. **3**, 1105 (1997)
	16	$^1\Sigma_u^+$ 31,056	Solution	Chem. Eur. J. **3**, 1105 (1997)
		$^1\Sigma_u^+$ 34,916	Gas	Chem. Phys. Lett. **393**, 225 (2004)
	18	$^1\Sigma_u^+$ 29,498	Solution	Chem. Eur. J. **3**, 1105 (1997)
NC$_n$N$^+$	2	A $^2\Sigma_g^+$ 9340	Gas	J. Chem. Phys. **123**, 144302 (2005)
(n even, X $^2\Pi_{g/u}$)		B $^2\Sigma_u^+$ 11,290		J. Chem. Phys. **129**, 134315 (2008)
(n odd, X $^2\Pi_{g/u}$)		C $^2\Pi_u$ 17,310		
		D $^2\Pi_u$ 33522		
	4	A$^2\Pi_g$ 16,780	Gas	J. Phys. Chem. **86**, 514 (1982)
		B$^2\Sigma_g^+$ 17,430		
		C $^2\Sigma_u^+$ 18,720		
NC$_n$N$^+$		D$^2\Pi_u$ 25,500		
n even X $^2\Pi_{g/u}$	6	A$^2\Pi_u$ 15,246	Gas	J. Chem. Phys. **71**, 3125 (1979)

(*continued*)

Table 3. Continued.

Species/electronic ground state	*n*	Origin (cm^{-1})	Phase	Reference
n odd X $^2\Pi_{g/u}$		$B^2\Sigma_g^+$, $C^2\Sigma_u^+$ 22,190		J. Chem. Phys. **116**, 924 (2002)
		$D^2\Pi_g$ 25,580		
		$E^2\Pi_u$ 30,420		
		$A^2\Pi_u$ 15173	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	7	15,897	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	8	$A^2\Pi_g$ 13,489	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	9	14,024	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	10	$A^2\Pi_u$ 12,029	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	11	12,587	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	12	$A^2\Pi_g$ 10,831	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
Panel C: HC_nN species				
HC_nN	2	a 4155	Gas	J. Chem. Phys. **117**, 4323 (2002)
n odd X $^1\Sigma^+$		$A^3\Sigma^-$ 41,667–29,412	Ar matrix	J. Chem. Phys. **66**, 4334 (1977)
n even X $^3\Sigma^-$	3	A^1A'' 38,485	Gas	J. Mol. Spectrosc. **19**, 155 (1966)
		$B^1\Delta/^1\Sigma^-$ 44,221	Gas	J. Mol. Spectrosc. **19**,178 (1966)
	6	$A^3\Sigma^-$ 21,209	Gas	J. Chem. Phys. **114**, 7918 (2001)
		$A^3\Sigma^-$ 21,181	Ne matrix	
HC_nN^+	3	A 15,650	Gas	Proc. Roy. Soc. (London). **A308**, 19 (1968)
n odd $^2\Pi$		B 19,600		
n even $^2\Pi$		C 48,570		
		B 19,374	Ne matrix	J. Phys. Chem. **89**, 3190 (1985)
	5	$A^2\Pi$ 17,178	Gas	J. Chem. Soc. Faraday Trans. **276**, 676 (1980)
		$B^2\Sigma^+$ 21860		J. Chem. Phys. **111**, 9600 (1999)
		$C^2\Pi$ 27350		

		$A^2\Pi$ 17,130	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	7	$A^2\Pi$ 14,925	Gas	J. Chem. Phys. **112**, 8899 (2000)
		$A^2\Pi$ 14,845	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	8	15,217	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	9	$A^2\Pi$ 12,978	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	10	13,395	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	11	$A^2\Pi$ 11,468	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	12	12,026	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
	13	$A^2\Pi$ 10,276	Ne matrix	J. Chem. Phys. **102**, 1510 (1995)
HC_nN^-	11	$^2\Pi$ 13,466	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
n odd $^2\Pi$		$^2\Pi$ 14,196		
n even $^2\Pi$		$^2\Pi$ 32,895		
	13	$^2\Pi$ 12,038	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 12,692		
		$^2\Pi$ 29,762		
	15	$^2\Pi$ 10,811	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 11,500		
		$^2\Pi$ 27,525		
	17	$^2\Pi$ 9745	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 10,611		
		$^2\Pi$ 25,562		
	19	$^2\Pi$ 8864	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 9950		
		$^2\Pi$ 25,562		
	21	$^2\Pi$ 8108	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 9413		
		$^2\Pi$ 22,437		
	23	$^2\Pi$ 7483	Ne matrix	J. Phys. Chem. A. **102**, 9785 (1998)
		$^2\Pi$ 28,952		

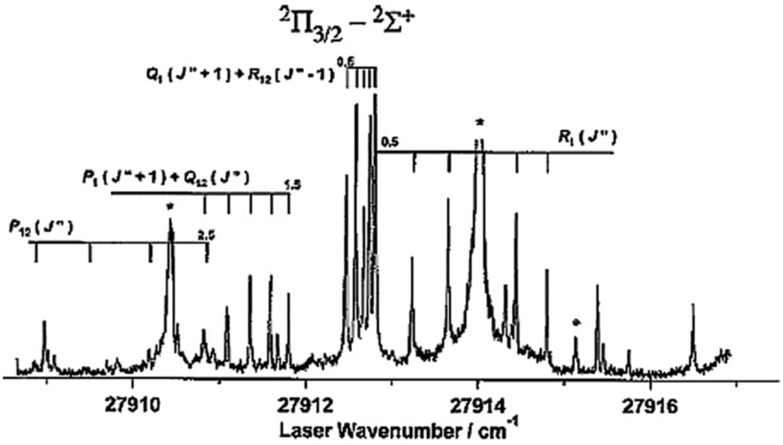

Figure 4. High-resolution laser induced fluorescence spectrum of the $^2\Pi_{3/2} \leftarrow X\ ^2\Sigma^+$ component of the origin band of the C_3N. The strong lines marked by asterisks are those of CN B $^2\Sigma^+ \leftarrow X\ ^2\Sigma^+$. Reproduced with permission from J. Chem. Phys. **127**, 184304 (2007).

Table 4. P terminated carbon chains: C_nP species.

Species/Electronic ground state	n	Origin (cm^{-1})	Phase	Reference
C_nP ($n \geq 2$, X $^2\Pi$)	2	$^2\Delta$ 15,898	Gas	J. Chem. Phys. **128**, 244311 (2008)

The ground state symmetries of even and odd-membered anions are known to be $^1\Sigma^+$ ($\pi^4\sigma^2$) and $^3\Sigma^-$ ($\pi^4\pi^2$), respectively. Recently, C_3N^- and C_5N^- were detected in the circumstellar envelope of IRC+10216 [57,58]. Spectra of the A $^1\Sigma^+ \leftarrow X\ ^1\Sigma^+$ transition of odd chains, $C_{2n-1}N^-$ ($n = 4$–7) have been measured in neon matrices. For the even chains, $C_{2n}N^-$ ($n = 1$–3), high-resolution photoelectron spectra have been recorded [59]. The results confirm that C_2N^-, C_4N^- and C_6N^- all have $^3\Sigma^-$ ground states. In addition, the corresponding neutrals have $^2\Pi_r$ ground states with a spin–orbit splitting of 38, 29 and 30 cm^{-1}, respectively. In the case of the cations, removal of one electron from either σ or π orbital corresponding to the odd and even neutral ground states results in a$^1\Sigma^+$ symmetry. Experimental data are only available for C_2N^+ where the IR and UV spectra for CCN^+ and CNC^+ in the X $^1\Sigma^+$ and A$^1\Pi$ states were measured in neon matrices (Table 3).

4.2. HC_nN, HC_nN^+ and HC_nN^-

Cyanopolyynes of the type $HC_{2n-1}N$ are closed shell species with $\pi^4\sigma^2$ electron configuration and $^1\Sigma^+$ ground states. Rotational spectra up to $HC_{17}N$ [60] have been measured by microwave spectroscopy and chains up to $HC_{11}N$ have been detected in space [61]. These studies confirm that the odd cyanopolyynes possess linear ground state geometry and show significant single–triple bond length alternation, much like the isoelectronic polyacetylenes, $HC_{2n}H$. In contrast, the ground state geometry in the even chains remains ambiguous due to competition between closely lying linear and ring chain isomers. For example, calculations [62,63] predict two stable isomers for HC_4N, the linear, $^3\Sigma^-$ and the $^1A'$ ring chain forms and three isomers for HC_6N, a triplet linear and two singlet ring chain structures. In HC_4N, the $^1A'$ is more stable by $20\,kJ\,mol^{-1}$ while in HC_6N, the linear $^3\Sigma^-$ is lower in energy by 10 and $16.7\,kJ\,mol^{-1}$, respectively, from the two $^1A'$ isomers. In two different mm wave studies, the ring chain structure has been observed for both species [64], while the linear isomer has been detected for HC_4N [65].

In the case of HC_2N, an electronic band system was observed in the 240–340 nm region in an argon matrix and tentatively assigned to the $A^3\Sigma^- \leftarrow X\ ^3\Sigma^-$ transition. In a combined matrix and CRD study, the origin band of the corresponding transition in HC_6N was detected around 471 nm and rotationally resolved. These transitions involve $\pi^* \leftarrow \pi$ excitation and show progressions in the acetylenic stretching mode. Similar features have been observed in the electronic spectra of NC_5N and HC_7H which are isoelectronic with HC_6N. Gas phase absorption spectrum of HC_3N revealed two-band systems in the UV, one corresponding to the linear–bent transition, $A^1A'' \leftarrow X\ ^1\Sigma^+$, similar to the 230 nm band system in acetylene and the other to a $^1\Delta$ or $^1\Sigma^+$ excited state, electronically forbidden, but made allowed by π-type vibrations.

The odd and even numbered cyanopolyyne anions have $^2\Pi$ ground states with a $\pi^4\pi^1$ or $\pi^4\pi^3$ configuration. Three band systems (A,B,C) $^2\Pi \leftarrow X\ ^2\Pi$ were observed for the $HC_{2n-1}N^-$ ($n = 7$–14) chains in neon matrices with the A and B systems overlapping in the near IR and the C state in the UV. The A and B states show strong origin bands which are separated by $730\,cm^{-1}$ in $HC_{11}N^-$ and move farther apart as the chain increases approaching $1305\,cm^{-1}$ in $HC_{21}N^-$. The B state gradually loses intensity with the chain length – this has been attributed to the decrease in the magnitude of vibronic interaction between the states as they move apart. For the three excited states, the band origin shifts to the red with number of carbon atoms, characteristic of $\pi \leftarrow \pi$ transitions. Among the cyanopolyacetylene cations, $HC_{2n-1}N^+$ ($n = 2$–7) and $HC_{2n}N^+$ ($n = 3$–6), electronic transitions have been observed in the gas phase and neon matrices. The origin bands of the A $^2\Pi \leftarrow X\ ^2\Pi$ systems in HC_5N^+ and HC_7N^+ have been rotationally resolved and analysed using frequency modulation absorption spectroscopy. Based on the rotational constants and molecular orbital consideration, it has been suggested that a reduction in the antibonding character of the C–C and bonding character of C≡C determine the structural changes upon ionisation to the X and A states of the cation. The ground X $^2\Pi$ state results from the removal of one electron from the π orbital of the neutral which is bonding in the C≡C regions and antibonding in the C–C regions resulting in a net contraction of the molecule and therefore a higher B_0 value than the neutral. In contrast, the A $^2\Pi$ state involves loss of an electron from the π orbital which is bonding in the outer C≡C regions and slightly bonding in the C–C region, resulting in a net increase in the chain length and smaller B_0 value than the neutral.

4.3. NC_nN and NC_nN^+

The dicyanopolyynes have linear ground state structures with $D_{\infty h}$ symmetry where the N atoms bond to the C atoms at the end of the chain. The even members, $NC_{2n}N$ have X $^1\Sigma_g^+$ (π_g^4/π_u^4) ground states while the odd systems have X $^3\Sigma_g^-$ (π_g^2/π_u^2) symmetry. These chains are thought of as resulting from a mixture of resonance structures with the even- and odd-numbered chains tending towards acetylenic and cummulenic forms, respectively [56,66]. UV absorption spectra have been measured for $NC_{2n}N$, $n = 1$–3, 8 in the gas phase and $n = 4$–9 in solution. In the case of $NC_{16}N$, the B $^1\Sigma_u^+ \leftarrow$ X $^1\Sigma_g^+$ transition was studied using a REMPI technique. The location of the band origin and the spectral profile closely resembled that of the isoelectronic $HC_{18}H$ indicating similar electronic structures. In addition, the ground and excited states A $^1\Sigma_u^+$, A $^1\Delta_u$ and B $^1\Sigma_u^+$ were investigated using time-dependent density functional theory. These studies suggest that in the $NC_{2n}N$ series, like the $HC_{2n}H$ chains, the single–triple bond length alternation is significant in the ground state and less pronounced in the excited state. Accordingly, the former assumes an acetylenic form whereas the latter are cumulenic in nature. For the odd numbered chains, the A $^3\Sigma_u^- \leftarrow$ X $^3\Sigma_g^-$ band system in NC_5N has been rotationally resolved using CRDS, while two excited states have been identified in argon matrices and assigned to NC_3N. The band origins and excited state symmetries are presented in Table 3, Panel B.

The even and odd dicyanopolyyne cations have X $^2\Pi_{g/u}$ ground states. For the even-numbered chains, the X $^2\Pi_{g/u}$ state can be described by $\sigma_u^2\sigma_g^2\pi_{g/u}^4\pi_{u/g}^3$ electron configuration. Promotion of an electron from the fully occupied inner π and σ orbitals to the HOMO gives $^2\Pi_{g/u}$, $^2\Sigma_g^+$ and $^2\Sigma_u^+$ excited states. Electronic excitation from the $\pi_{u/g}^3$ HOMO to $\pi_{g/u}$ LUMO results in $^2\Pi_{g/u}$ states which lie higher in energy; these have been tabulated in Table 3, Panel B. Recently, the B $^2\Sigma_u^+ \leftarrow$ X $^2\Pi_g$ absorption spectrum of NC_2N^+ was measured in an ion trap using a two-colour, two-photon dissociation technique. Figure 5 depicts the absorption spectrum recorded at ~20 K and 0.3 cm^{-1} resolution, showing excitation of four normal modes; $\nu_1(\sigma_g^+)$, $\nu_2(\sigma_g^+)$, $\nu_4(\pi_g)$ and $\nu_5(\pi_u)$. The A $^2\Pi_u \leftarrow$ X $^2\Pi_g$ transition of NC_6N^+ has been rotationally analysed using frequency modulation absorption technique. Spectral perturbations characteristic of Λ-type doubling and an estimation of the second order spin–orbit splitting parameter of the A $^2\Pi_u$ state was used to identify and locate the unobserved $^2\Sigma_g^+$, 208 cm^{-1} below the A state. The first excited A $^2\Pi$ state has been identified in neon matrices for $NC_{2n}N^+$, $n = 3$–6 along with unassigned states for $NC_{2n-1}N^+$, $n = 4$–6.

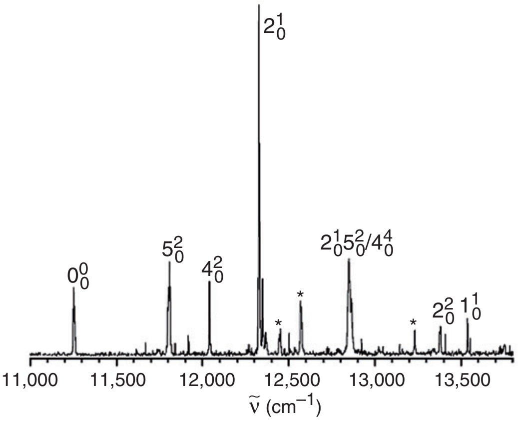

Figure 5. Resonant two-colour, two-photon spectrum of the B $^2\Sigma_u^+ \leftarrow$ X $^2\Pi_{3/2,g}$ transition in a 22-pole ion trap at 20 K recorded by monitoring CN^+ as the photo-dissociation product.

4.4. C_nP, C_nP^+ and C_nP^-

In contrast to the nitrogen doped carbon chains, information on the electronic structure of the isovalent phosphorous terminated systems is scarce. The role of P containing molecules in the ISM attracted much attention following the detection of PN [67,68] and PC [69] in space. C_2P and HC_2P were predicted to be present in the warm dense clouds with the former being recently detected in IRC + 10216 [70]. Theoretical study of C_nP, C_nP^+ and C_nP^- ($n = 1$–7) [71] predict that these molecules assume a linear $C_{\infty v}$ ground state geometry with the phosphorous atom located at the end of the carbon chain. With the exception of CP which has a $^1\Sigma^+$ ground electronic state, the other members possess $^2\Pi$ electronic ground state. The corresponding ions show odd/even alternation in the ground state symmetry; with $^1\Sigma^+$ (n odd)/$^3\Sigma^-$ (n even) for C_nP^- and $^3\Sigma^-$ (n odd)/$^1\Sigma^+$ (n even) for C_nP^+. Among the phosphorous terminated systems with $n \geq 2$, C_2P is the only radical where the electronic structure has been experimentally investigated. Recently, a LIF spectrum of the $^2\Delta \leftarrow X\,^2\Pi$ transition of C_2P (Table 4) was recorded and RT parameters for the ground and excited states were deduced. An allenic structure for the ground state has been inferred following rotational analyses of the two spin–orbit components of the origin band.

5. Oxygen terminated carbon chains

5.1. C_nO, C_nO^+ and C_nO^-

Carbon monoxide is the second most abundant molecular species in space following hydrogen. The next higher members, C_2O and C_3O have been detected in TMC-1 [72,73], thereby triggering the radio astronomical search for the longer chains in this family of polycarbon oxides. In terrestrial environment, the ground electronic states of C_nO ($n = 2$–9) have been investigated by microwave spectroscopy [74–76]. These studies have demonstrated that C_nO's have linear ground state geometries with cumulenic bonds where ground state alternates between $^3\Sigma^-$ (π^2) for even and $^1\Sigma^+$ (π^4) for the odd chains. In addition, electron spin resonance spectra in low-temperature matrices measured for C_2O, C_4O and C_6O support the above assignment. For the even chains, the π^2 electron configuration also gives rise to $^1\Sigma^+$ and $^1\Delta$ states. In the microwave investigation on C_nO ($n = 2$, 4, 6, 8) [75], the spin–spin coupling parameter for the triplet state was deduced and was seen to increase rapidly with n. It was concluded that the dominant contribution was from the second-order spin–orbit coupling term which mixes the $^3\Sigma^-$ and $^1\Sigma^+$ states. As a result, the energy difference between these states tends to decrease with an increase in the chain length. The $^1\Sigma^+$ state for $n = 2$, 4 and 6 has been predicted to lie around 1.10, 0.47 and 0.11 eV above the ground state. In an anion photodetachment study on C_2O^- [77], the $^1\Sigma^+$ was identified and located around 1.01 eV above the triplet state. In addition, term energies of the $^1\Delta$ and $^3\Pi$ states were determined as 0.65 and 1.44 eV, respectively. The first optically allowed A $^3\Pi \leftarrow X\,^3\Sigma^-$ transition has been observed by LIF (Table 5, Panel A) in which the upper state was found to be RT active; the ground and excited state molecular parameters were deduced from their rotational spectra.

The $C_nO^\pm$ are expected to have linear ground state geometries with the even/odd-numbered cations and anions exhibiting $^2\Pi_r$ (π^1)/$^2\Pi_i$ (π^3) and $^2\Pi_i$ (π^3)/$^2\Pi_r$ (π^1) symmetries, respectively. There is a lack of experimental information on the electronic structure of the C_nO cations. In contrast, the smaller anions have been studied by matrix isolation (C_2O^-, C_4O^-) and photoelectron (C_2O^-, C_3O^- and C_4O^-) spectroscopy [77–80]. The A $^2\Sigma^+ \leftarrow$ X $^2\Pi$ (C_2O^- and C_4O^-) and the B $^2\Pi \leftarrow$ X $^2\Pi$ (C_4O^-) transitions have been observed in neon matrices. A spin–orbit splitting of 65 cm^{-1} in X $^2\Pi_i$ of C_2O^- has been deduced from photoelectron studies [77]; in a separate investigation, C_3O^- was shown to have a bent equilibrium ground state [80].

5.2. *HC_nO, HC_nO^+ and HC_nO^-*

The hydrogen substituted C_nO's have received attention due to their role in combustion processes [81] and interstellar chemistry [82]. HC_2O in particular has been recognised as a key intermediate in the oxidation of acetylene which ultimately results in the production of carbon dioxide. The geometrical structures of HC_nO ($n = 1$–7) have been characterised by studies in the mm and sub-mm regions [83–85]. The lower members with $n = 1$–4 are reported to have bent planar geometries with HC_3O and HC_4O being bent at the CCO subunit while HC_2O assumes a bent HCC structure. These radicals are subjected to strong RT interaction where the ground state alternates between $^2A'$ for n odd and $^2A''$ for n even which correlate with the Π state in the linear configuration. This energy difference has been estimated to be around 540 cm^{-1} for HC_2O and 2560 cm^{-1} for HC_3O. In contrast, the higher members with $n = 5$, 6 and 7 are found to have linear structures with $^2\Pi$ ground states which alternate between $^2\Pi_{3/2}$ for n even and $^2\Pi_{1/2}$ for n odd.

In the case of HC_2O, the next higher state assigned to the linear B $^2\Pi_i$ has been observed by LIF spectroscopy. The spectrum revealed a progression in the ν_3, CCO stretching mode and several other bands which were attributed to excitation of the RT active CCH and CCO bending modes in the excited state. In addition, the spin–orbit splitting in the B $^2\Pi_i$ state was deduced to be -46.73 cm^{-1}. Experimental data on the ground and excited states of the corresponding anions and cations have not been reported thus far.

5.3. *OC_nO*

Among the polycarbon dioxides, electronic absorption spectra have been measured for the neutrals. In the linear configuration, the odd and even members of this group are expected to have $^1\Sigma^+$ (π^4) and $^3\Sigma^-$ (π^2) ground electronic states, respectively. The vacuum UV spectra of carbon suboxide, C_3O_2 is dominated by an intense broad continuum around 159 nm, a band system around 178 nm assigned to the $^1\Sigma_u^+ \leftarrow$ X $^1\Sigma_g^+$ transition and a weak continuum around 270 nm. UV absorption bands of the higher members have been observed in argon matrices and the wavelength positions are presented in Table 5, Panel C. Recently, the IR and UV-Vis spectra of OC_nO and C_nO ($n = 9, 11, \ldots, 21$) trapped in low temperature matrices were experimentally and theoretically investigated. Electronic absorptions around 397 and 452 nm were tentatively assigned to $C_{13}O$ and $C_{15}O_2$, respectively. The result from this study [86] also indicated that the polycarbon oxides possess strong electronic absorptions which lie in the vicinity of the corresponding bare carbon chains.

Table 5. O terminated carbon chains.

Species/electronic ground state	n	Origin (cm^{-1})	Phase	Reference
Panel A: C_nO species				
C_nO	2	a$^1\Delta$5242	Gas	J. Chem. Phys. **129**, 074312 (2008)
n even X $^3\Sigma^-$		b$^1\Sigma^+$ 8416		J. Chem. Phys. **108**, 4070 (1998)
n odd X $^1\Sigma^+$		A$^3\Pi$ 11,614		Chem. Phys. **61**, 451 (1981)
		c$^1\Pi$ 22,390		
C_nO^-	2	A$^2\Sigma^+$12234	Ne matrix	J. Phys. Chem. A. **102**, 3459 (1998)
n even X $^2\Pi$	4	A$^2\Sigma^+$ 11434	Ne matrix	J. Phys. Chem A. **105**, 4894 (2001)
n odd X $^2\Pi$		B$^2\Pi$ 22610		
Panel B: HC_nO species				
HC_nO	2	B$^2\Pi$ 33,465	Gas	J. Chem. Phys. **110**, 6773 (1999)
n even X ^{2}A″				
n odd X ^{2}A′				
Panel C: OC_nO species				
OC_nO	3	$^1\Sigma^+$ 56,179	Gas	J. Mol. Spectrosc. **21**, 42 (1996)
n even X $^3\Sigma^-$	4	47,200	Ar matrix	Angew. Chem. **102**, 920 (1990)
n odd X $^1\Sigma^+$	5	43,500	Ar matrix	Angew. Chem. **27**, 566 (1998)
	6	39,682	Ar matrix	Tetrahed. Lett. **32**, 4469 (1991)
	7	34,720	O_2 matrix	J. Phys. Chem. A. **110**, 12395 (2006)
	15	22,123	O_2 matrix	J. Mol. Spectrosc. **243**, 189 (2007)

6. Sulphur terminated carbon chains

6.1. C_nS, C_nS^+ and C_nS^-

The fractional abundance of sulphur in space is lower than oxygen; however, polycarbon sulphides C_2S and C_3S have been detected via radio astronomy in the dense molecular cloud TMC-1 [87], and are found to be present in greater abundance than the isovalent species, C_2O and C_3O. In addition, these have been identified in the outer envelopes of IRC + 10216 along with C_5S [88,89]. It has been postulated that the hydrogenated counterparts may be present in detectable abundances as well. The symmetrical species, SC_nS however, lack a permanent dipole moment and cannot be detected via radio astronomy, but can be observed by their infrared or electronic absorptions.

The neutral C_nS species show an alternation in the ground state symmetry. The even and odd numbered chains can be differentiated by $^3\Sigma^-$ (π^2) and $^1\Sigma^+$ (π^4) whereas the even/odd cations have $^2\Pi_r$ (π^1)/$^2\Pi_i$ (π^3) and the anions show $^2\Pi_i$ (π^3)/$^2\Pi_r$ (π^1) ground states. DFT calculations have been performed on neutrals up to $n = 20$ and the ground state geometries have been compared with the bare carbon chains [90]. These studies indicate that the C_nS molecules are linear up to $n = 17$ beyond which there is a substantial decrease in the energy difference between the linear and cyclic forms. The latter is more stable by 24.3 kJ/mol for $n = 18$, while $n = 19$, 20 are linear. In contrast, the carbon species are predominantly linear up to $n = 10$ while the larger members assume cyclic structures. This has been attributed to the divalent nature of sulphur as opposed to the tetravalent one of carbon. As a result, sulphur takes up the terminal position of a C-chain where it is doubly bonded to the adjacent carbon, while in the cyclic structure; it lies outside the ring and forms two single bonds with two neighbouring carbon atoms. This preference to linearity has been observed in the anions and cations as well [91]. Linear structures have been predicted for anion chains up to $n = 16$ and $n = 14$ for cations. In $C_{15}S^+$ and $C_{16}S^+$, the cyclic structure is more stable by 0.08 and 0.27 eV, respectively. The bonding in these chains is found to be cumulenic in nature.

Experimentally, C_nS ($n = 2$–9) have been investigated by microwave spectroscopy [92–94]. In addition, IR spectra have been recorded in argon matrices for $n = 1$–5 [95,96]. Information on the excited electronic states in neutral and anionic chains is presented in Table 6, Panel A. However, electronic spectra of the cationic species have not been reported thus far. The $^1\Sigma^+ \leftarrow X\ ^1\Sigma^+$ transition for C_nS ($n = 3$, 5), $^3\Sigma^- \leftarrow X\ ^3\Sigma^-$ ($n = 2$, 4

Table 6. S terminated carbon chains.

Species/electronic ground state	n	Origin (cm^{-1})	Phase	Reference
Panel A: C_nS species				
C_nS	2	$^3\Pi$ 9146	Ne matrix	J. Mol. Spectrosc. **222**, 15 (2003)
n even X $^3\Sigma^-$		$^3\Sigma^-$ 30,563		
n odd X $^1\Sigma^+$		$^3\Pi$ 9226	Gas	J. Chem. Phys. **117**, 9327 (2002)
		$^3\Sigma^-$ 30,627		J. Chem. Phys. **130**, 014302 (2009)
	3	26,460	Ar matrix	Chem. Ber. **124**, 2617 (1991)
	4	$^3\Sigma^-$ 22,380	Ne matrix	J. Phys. Chem A. **105**, 4894 (2001)
	5	$^1\Sigma^+$ 35,169	Ne matrix	J. Phys. Chem A **107**, 8856 (2003)
	6	$^3\Sigma^-$ 17,416	Ne matrix	J. Phys. Chem A. **107**, 8856 (2003)
C_nS^-	2	$^2\Sigma^+$ 10,606	Ne matrix	J. Mol. Spectrosc. **222**, 15 (2003)
n even X $^2\Pi$		$^2\Pi$ 22,273		
n odd X $^2\Pi$	4	$^2\Pi$ 17,593	Ne matrix	J. Phys. Chem A. **105**, 4894 (2001)
	6	$^2\Pi$ 16,447	Ne matrix	J. Phys. Chem A. **105**, 4894 (2001)
Panel B: SC_nS species				
SC_nS	2	A 25,510	Ar matrix	J. Am. Chem. Soc. **114**, 6452 (1992)
n even X $^3\Sigma^-$		B 43,500		
n odd X $^1\Sigma^+$	3	A 430–530 nm	Gas	J. Chem. Phys. **56**, 5428 (1972)
		B 220–255 nm		
	4	A 19,455	Gas	Chem. Ber. **124**, 2617 (1991)
		B 36,765		
	5	A 15,100	Gas	Chem. Ber. **123**, 1753 (1990)
		B 31,250		
SC_nS^-	2	$^2\Pi$ 18,423	Gas	Chem. Phys. Lett. **410**, 172 (2005)
n even X $^2\Pi$				
n odd X $^2\Pi$				
Panel C: HC_nS species				
HC_nS	2	$^2\Pi_{3/2}$ 24,197	Gas	J. Chem. Phys. **123**, 014317 (2005)
X $^2\Pi_{3/2}$ (n even)	4	$^2\Pi_{3/2}$ 19,981	Gas	Phys. Chem. Chem. Phys. **10**, 136 (2008)
	6	$^2\Pi_{3/2}$ 16,961	Gas	Int. J. Mass. Spectrom. **233**, 131 (2004)
	8	$^2\Pi_{3/2}$ 14,838	Gas	Int. J. Mass. Spectrom. **233**, 131 (2004)
	10	$^2\Pi_{3/2}$ 13,334	Gas	Int. J. Mass. Spectrom. **233**, 131 (2004)

and 6) and A $^3\Pi \leftarrow X\ ^3\Sigma^-$ for C_2S have been observed in 6 K neon matrices. The gas phase LIF spectra of the corresponding band systems in C_2S have been recorded and rotationally resolved. In the case of the anions, B $^2\Pi \leftarrow X\ ^2\Pi$ transition for $n = 2$, 4 and 6 and the $A^2\Sigma^+ \leftarrow X\ ^2\Pi$ for $n = 2$ have been observed in neon matrices. In addition, C_2S^- and C_3S^- have been investigated via anion photoelectron spectroscopy [77,80]. In the case of C_2S, two low-lying singlet states, a $^1\Delta$ and $b^1\Sigma^+$ have been located at 0.45 and 0.74 eV above the X $^3\Sigma^-$ ground state. The spin–orbit splitting for the anion ground state, X $^2\Pi_i$ was around 195 cm^{-1}. In the case of C_3S^-, the photoelectron spectrum revealed a strong progression in the ν_4 bending mode indicating bent and linear equilibrium geometries for the anion and neutral, respectively.

6.2. *HC_nS, HC_nS^+ and HC_nS^-*

The hydrogenated polycarbon sulphides, HC_nS are open shell species with $^2\Pi$ ground states in which the spin–orbit and RT effects play crucial roles towards understanding their electronic structure. The ground state geometries and electronic structure for $n = 2$–8 have been investigated via microwave spectroscopy [97–99]. These studies confirm that the HC_nS chains have linear structures with the even and odd chains exhibiting $^2\Pi_i$ (π^3) and $^2\Pi_r$ (π^1) symmetries, respectively, in contrast to the isovalent HC_nO species which have bent equilibrium geometries. In a recent theoretical study, the spin–orbit coupling in the $^2\Pi$ ground state for HC_nS ($n = 1$–12) was calculated and determined to be around -300 cm^{-1} for the even and 120 cm^{-1} for the odd numbered chains [100].

In the above series, the even members with $n = 2$, 4, 6, 8 and 10 have been investigated by optical spectroscopy in the gas phase (Table 6, Panel C), with HC_2S being extensively studied both experimentally and theoretically. The LIF spectra of the $^2\Pi_i \leftarrow X\ ^2\Pi_i$ transition for $n = 2$, 4 and 6 have been recorded. In the case of HC_2S, spectral analysis yielded ground and excited state spin–orbit splitting of -254.1 and 45.4 cm^{-1}, respectively. In addition, the excited state was found to be quasilinear based on the large RT splitting. Recently, the $^2\Pi_{3/2} \leftarrow X\ ^2\Pi_{3/2}$ transition of HC_2S and HC_4S was recorded in a supersonic slit-jet discharge using degenerate four-wave mixing and two-colour resonant four-wave mixing (TC-RFWM) techniques. Figure 6 depicts the method and assignment procedure for the rotational lines of the TC-RFWM spectrum of $A^2\Pi_{3/2} \leftarrow X\ ^2\Pi_{3/2}$ transition in HC_2S. Using this approach, 14 vibrational levels of the X $^2\Pi_{3/2}$ ground state were rotationally resolved with a high signal-to-noise ratio of $\sim 10^3$. The above band system has been recorded for HC_6S by R2PI and HC_8S and $HC_{10}S$ by CRD spectroscopy. A near linear relationship was observed between the absorption wavelength and the chain size, similar to the C_nH^- chains, suggesting cumulenic bonding. The band origin of the next higher member, $HC_{12}S$ has been estimated to be around 820 nm.

Experimental and theoretical data on the corresponding cations and anions is sparse. HC_nS ions have been generated by laser ablation of a mixture of carbon and sulphur and the products analysed by collision induced dissociation and *ab inito* calculations. The structure of the ions was found to be linear with the hetero atoms located at the ends of the chain. These studies also suggest that the weakest bond is the C–C bond adjacent to the terminal sulphur atom [101].

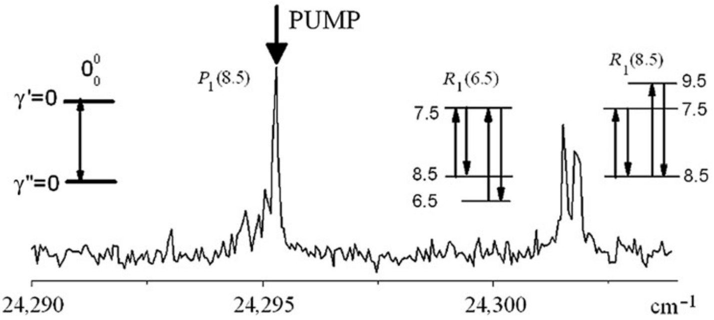

Figure 6. Two-colour resonant four wave mixing (TC-RFWM) spectrum of HC_2S recorded by fixing the pump laser at the $P_1(8.5)$ transition of the origin band of A $^2\Pi_{3/2} \leftarrow$ X $^2\Pi_{3/2}$ band and scanning the pump laser through the 0^0_0 transition. The nearly degenerate TC-RFWM displays three transitions: the degenerate transition at $P_1(8.5)$ and two R_1 transitions sharing the upper and lower level ($R_1(6.5)$ and $R_1(8.5)$, respectively).

6.3. SC_nS and SC_nS^-

The SC_nS chains, like the C_nS species show an even–odd alternation in the ground state symmetry, with the even and odd members represented by $^3\Sigma^-$ (π^2) and $^1\Sigma^+$ (π^4), respectively. Information on the ground state geometry, vibrational frequencies and the favourable dissociation pathways in clusters up to $n = 29$ have been deduced using the DFT method [96]. The results indicate that these chains have linear ground states and are cumulenic in nature. The dissociation energies of SC_nS with odd n were higher than the even n, suggesting that the odd numbered chains are more stable. This is consistent with the complete occupancy of the π orbital in these chains. In addition, the most favoured dissociation channel was the loss of CS species.

Electronic spectra have been recorded for $n = 2$–5 in the vapour phase and argon matrices (Table 6, Panel B). Two-band systems, one in the visible and the other in the UV were observed. In the case of C_3S_2, phosphorescence from the $^3\Sigma_u^-$ state located around 18,287 cm^{-1} was observed in argon matrices. Among the anions, LIF spectrum of A $^2\Pi_g \leftarrow$ X $^2\Pi_u$ band system in $C_2S_2^-$ has been recently measured. This is the only other anion, besides C_2^- [102] and C_4^- [103] for which fluorescence measurements are known. From the fluorescence depletion and dispersed emission measurements the C–C and C–S stretching frequencies for the ground and excited states were deduced. The A $^2\Pi$ ($v' = 0$) state was found to have a lifetime of ~30 ns consistent with the theoretically predicted value of 20 ns leading to the conclusion that the fluorescence quantum yield is approximately unity for the vibrationless level of the A state.

7. Metal terminated carbon chains

Alkaline earth metal acetylides, MC_2H; M=Mg, Ca, Sr are known to have $^2\Sigma^+$ ground states, where the unpaired electron is located in a sigma orbital which is predominantly metal *ns* in character. The electro-positive nature of the alkaline earth metals and the high electron affinity of the C_2H radical (2.9 eV) results in a chemical bond (M–C_2H) which can be described as being ionic. The electronic structure and bonding in these systems are

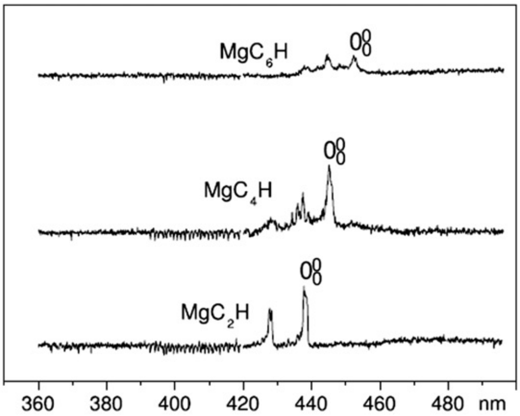

Figure 7. Resonant two-colour, two-photon ionisation spectra of the A $^2\Pi \leftarrow X\ ^2\Sigma^+$ electronic transition of MgC$_{2n}$H ($n = 1$–3).

similar to the corresponding well-characterised hydrides, halides and hydroxides. Pure rotational spectra have been recorded for MgC$_2$H [104], CaC$_2$H [105] and SrC$_2$H [106] which confirm a linear $^2\Sigma^+$ ground state. The lowest electronic states have $^2\Sigma^+$, $^2\Pi$ and $^2\Delta$ symmetries with major contributions from the metal ns, np and $(n-1)$d orbitals.

The A $^2\Pi \leftarrow X\ ^2\Sigma^+$ transition has been observed in the three acetylides and the higher members of the MgC$_n$H series ($n = 4$, 6) as well (Table 7). The $\pi \leftarrow \sigma$ electron excitation corresponding to the above transition revealed a strong progression in the M–C stretching mode. The stretching frequency was found to be higher for the excited state indicating a decrease in the bond length upon excitation. In addition, the f values for the A $^2\Pi \leftarrow X\ ^2\Sigma^+$ and B $^2\Pi \leftarrow X\ ^2\Sigma^+$ transitions calculated using the TD-DFT method for MgC$_{2n}$H ($n = 1$–8) were found to decrease with the chain length [107]. These characteristics have been explained in terms of promotion of an electron from the metal centred σ HOMO which is antibonding in character, to the π LUMO, composed mainly of metal np orbitals. This results in a stronger M–C bond in the excited state, moreover, as the chain length increases, the σ electron becomes more delocalised resulting in a decrease in the f value. The REMPI spectrum of the A $^2\Pi \leftarrow X\ ^2\Sigma^+$ electronic transition of MgC$_{2n}$H ($n = 1$–3) is shown in Figure 7. The B $^2\Sigma^+ \leftarrow X\ ^2\Sigma^+$ (CaC$_2$H) and the orbitally forbidden C $^2\Delta \leftarrow X\ ^2\Sigma^+$ (CaC$_2$H and SrC$_2$H) transitions have been observed by CRDS and LIF. In the case of AlC$_2$H, DFT calculations predicted two structures; the linear and cyclic isomers, with the former being stable by 41 kJ mol^{-1}. Recently, aluminium monoacetylide was investigated using a REMPI technique. The rotationally resolved spectrum corresponding to the origin band is displayed in Figure 8. Based on the analysis, the spectrum was assigned to the A $^1\Pi \leftarrow X\ ^1\Sigma^+$ transition of linear AlC$_2$H.

The other metal terminated carbon chains with known optical transitions include AlC$_2$ and SiC$_2$ with the latter having been detected in IRC + 10216 [108,109]. By analogy to C$_3$, SiC$_2$ was thought to possess a linear structure. However, rotationally resolved R2PI studies confirmed a T-shaped cyclic structure (C$_{2v}$); a three-membered ring with C≡C triple bond corresponding to a X $^1A_1$ ground state. The linear isomer (C$_{\infty v}$) has been predicted to lie around 25 kJ mol^{-1} higher in energy [110]. Among the larger members,

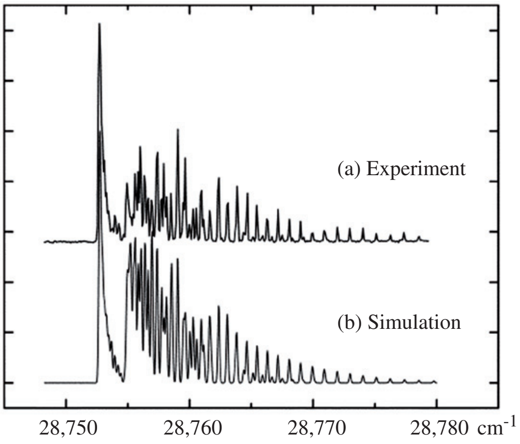

Figure 8. (a) Experimental and (b) simulated spectra corresponding to the origin band of the $A^1\Pi \leftarrow X\ ^1\Sigma^+$ electronic transition for AlCCH measured using the resonant two-colour two-photon ionisation technique.

cyclic SiC_3 [111] and linear SiC_4 [112] have been detected in the circumstellar media. Pure rotational spectra of linear SiC_n ($n = 3$ and 5–8) chains have been recorded which confirm an even/odd alternation in the ground state symmetry; $^1\Sigma^+$ for the even n chains and $^3\Sigma^-$ for the odd n systems [113]. The corresponding anions SiC_n^- ($n = 3$–7) have been investigated by photoelectron spectroscopy and are shown to possess a linear $C_{\infty v}$ ground state geometry [114,115]. Like silicon dicarbide, AlC_2 exhibits a cyclic structure ($X\ ^2A_1$) which is more stable than the linear ($X\ ^2\Sigma^+$) isomer by 33 kJ mol^{-1} [116] (46 kJ mol^{-1}) [117]. In the case of AlC_2, bonding has been explained in terms of electron donation from the more electropositive Al to the electronegative C_2 via σ and π coordination. The first excited A^1B_2 state has been experimentally observed for SiC_2 and higher electronic states with $^1A_1$ and $^1B_1$ symmetries have been predicted. The lowest excited $^2A_1$ in AlC_2 was detected around 1260 nm by photoelectron studies. Recently, the $C\ ^2B_2 \leftarrow X\ ^1A_1$ and $D\ ^2B_1 \leftarrow X\ ^1A_1$ were rotationally analysed by LIF and REMPI.

8. Outlook

Over the years, researchers have employed a variety of experimental techniques to record electronic spectra of carbon chains and ions. This has created a wealth of data which continues to grow. Initial measurements carried out on mass selected species condensed in argon or neon matrices have been the guiding tools for further gas phase measurements. Spectra recorded in the gas phase using supersonic expansion or by buffer gas cooling of trapped ions are associated with internally cold molecules and are also free of matrix perturbations. This is crucial for direct comparisons with astrophysical observations. The above methodology has been successfully implemented on bare carbon chains, their hydrogen and nitrogen derivatives leading to a general consensus that C-chains with less than 10 carbon atoms cannot be carriers of DIB absorptions that lie in the 400–900 nm range. Instead, closed shell species ($^1\Sigma^+$) such as the longer odd carbon chains

Table 7. Metal terminated carbon chains: MC_nH/MC_n species.

Species/electronic ground state	n	Origin (cm^{-1})	Phase	Reference
MgC_nH	2	A $^2\Pi$ 22,809	Gas	J. Mol. Spectrosc. **230**, 54 (2005)
X $^2\Sigma^+$	4	A $^2\Pi$ 22,450	Gas	ApJ. **677**, 348 (2008)
	6	A $^2\Pi$ 22,093	Gas	ApJ. **677**, 348 (2008)
CaC_nH	2	A $^2\Pi_{1/2}$ 15,487	Gas	Chem. Phys. Lett. **136**, 97 (1987)
X $^2\Sigma^+$		A $^2\Pi_{3/2}$ 15,560		
		B $^2\Sigma^+$ 16,567	Gas	Chem. Phys. Lett. **433**, 264 (2007)
		C $^2\Delta$ 22,157	Gas	Chem. Phys. Lett. **288**, 785 (1998)
SrC_nH	2	A $^2\Pi_{1/2}$ 14,176	Gas	Chem. Phys. Lett. **136**, 97 (1987)
X $^2\Sigma^+$		A $^2\Pi_{3/2}$ 15,560		
		B $^2\Delta_{3/2}$ 21,077	Gas	J. Mol. Spectrosc. **206**, 198 (2001)
		B $^2\Delta_{5/2}$ 21,183		
AlC_nH	2	A $^1\Pi$ 28,750	Gas	Phys. Chem. Chem. Phys. **9**, 3897 (2007)
X $^1\Sigma^+$				
AlC_n	2	A $^2A_1$ 7910	Gas	J. Am. Chem. Soc. **121**, 10193 (1999)
X^2A_1		C $^2B_2$ 22,098		J. Chem. Phys. **131**, 064305 (2009)
		D $^2B_1$ 26,073		
SiC_n	2	A $^1B_2$ 20,080	Gas	J. Chem. Phys. **80**, 3556 (1984)
X^1A_1				

$C_{17}, C_{19}, \ldots, C_{2n+1}H^+$, $C_{2n}N^+$, $C_{2n+1}O$ and related molecules which have strong $^1\Sigma^+ \leftarrow X\ ^1\Sigma^+$ transitions in the DIB range remain as viable candidates. Gas phase spectroscopy of sulphur bearing carbon chains isovalent with the C_nO systems and metal terminated (Si, Fe, Mg and Al) carbon chains would be a worthwhile endeavour.

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