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Carbon chains are of interest in astrophysics and in terrestrial processes, such as fullerene formation. The electronic spectra of a variety of such chains have now been identified in the laboratory using a technique which enables absorption spectra of mass-selected species to be measured in neon matrices. The understanding of their transitions and the trends apparent for these homologous series point out which type and size of carbon chains are relevant for consideration as carriers of the diffuse interstellar bands.

1 Introduction

Spectroscopic characteristics of carbon species are desirable not only as basic knowledge, but are necessary in the interpretation of astronomical observations. The availability of laboratory spectra led in the past to the identification of the simple carbon molecules C_2 and C_3 in comets *via* their electronic transitions as well as to long polycyanoacetylene chains in dark clouds by microwave spectroscopy.¹ Also in terrestrial chemical processes, such as the formation of fullerenes, carbon chains are postulated as precursors.² Thus, an understanding of their spectroscopic properties is prerequisite to the study of their reaction mechanisms in the laboratory.

This goal to observe and assign the spectra of carbon chains, and their isoelectronic species involving nitrogen and hydrogen, has only recently been realized. It has come about as result of the development of a technique which enables the electronic absorption spectra of mass-selected species in neon matrices to be measured.³

Prior to this, the electronic transitions of only C_2 , C_3 , C_2^- and C_2^+ in the gas phase had been known.⁴ On the other hand, rotationally resolved infrared spectra of the carbon chains C_n in the range $n = 3-13$ have been obtained in recent years.⁵ Several studies of carbon vapour condensed in rare gas matrices have

been reported with some suggested assignments to specific species.^{6,7} This has been plagued with uncertainty due to the concomitant presence of a number of species. We could circumvent this handicap by conducting such measurements on mass-selected species and this has resulted in the identification of the characteristic $\pi-\pi$ electronic transitions of a variety of carbon chains, neutral and ionic.

These observations allow the relevance of specific species to astrophysical measurements to be discussed and indicate the directions to be pursued in trying to identify the molecules likely to be responsible for the diffuse interstellar bands.⁸ These are spectral features due to starlight absorption by molecules present in interstellar space, but their identification has remained a mystery for over half a century. It is one of the aims of spectroscopic studies on the carbon chains to establish whether these could be the carriers responsible. Because the electronic transitions in the neon matrix have been observed, measurement of the spectra in the gas phase has become a realistic proposition.

2 Approach

The difficulties in trying to measure the spectra of transient species in the gas-phase, the ultimate goal, are threefold — their generation in sufficient concentration, availability of a sensitive approach to measure their spectrum and knowledge of the energy region of the transitions are required. We have now developed a technique which combines the virtues of mass- and matrix isolation-spectroscopies.³ Mass-selection alleviates the need to identify the absorbing species, whereas the neon matrix enables sufficient concentrations of ions and radicals to be attained so that direct absorption measurements can be made. The philosophy is then to identify the electronic transitions of a chosen species in the inert neon environment, and with this knowledge in hand to attempt a gas-phase characterization. The studies of the carbon species in the gas phase C_2^{+9} and recently C_{2n-} $n = 2,3,4$,¹⁰ were only realised once the electronic transitions were identified in the neon matrix.¹¹

3 Experimental considerations

Matrix isolation spectroscopy is a well-established technique, and neon matrices show the smallest energy shifts relative to the gas-phase.¹² An experimental advantage compared to traditional matrix spectroscopy where relatively thick matrices tend to be grown on sapphire substrates, and measurements follow as transmission, is the implementation of a waveguide technique.¹³ This enables matrices 150 μm thick to be grown in approximately two hours and the probing light is propagated through the thin side along the 2 cm length of the matrix. For this purpose the matrices are grown on copper substrates coated with rhodium, providing good reflectivity from the UV to IR.

The other half of the instrument provides a mass-selected ion beam. Experience has shown that ion currents of more than 1 nA are necessary for the recording of the absorption spectra. Thus, the ion source is a crucial element — hot cathode discharge and a caesium sputter source have been used.¹⁴ Electron lenses and a high transmission quadrupole mass-spectrometer steer the ion beam onto the matrix. In Fig. 1 the overall arrangement of the instrument is depicted.

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Codeposition of the mass-selected ions, usually with nominal kinetic energies 50–200 eV, with excess of neon leads to matrix formation with ion densities in the $10^{15-16} \text{ cm}^{-3}$ range. This is sufficient for the absorption spectra to be discernible. The waveguide approach is used in the 220–1000 nm region, and a reflection method using a Fourier transform instrument, though with an order of magnitude less sensitivity, covers the near IR.

4 Electronic structure considerations

The lowest energy, strong electronic transitions encountered in the carbon chains involve the excitation of π electrons. The open-shell species, polyacetylene cations, HC_nH^+ , and the isolectronic chains, C_nH , C_n^- , have the ground state configuration π^3 and thus $X^2\Pi$ symmetry. The excited states of relevance are the ones corresponding to $\pi-\pi$ electron promotion, resulting in $^2\Pi-X^2\Pi$ electronic transitions.

In the case of the bare carbon chains, C_n , the species are paramagnetic for $n = \text{even}$ but not for $n = \text{odd}$.¹⁵ The former have triplet ground states, $X^3\Sigma_g^-$ arising from the configuration

π^2 . The characteristic transition has $^3\Sigma_u^- - X^3\Sigma_g^-$ symmetry, to which configurations arising from both $\pi^*-\pi$ and $\pi-\pi$ excitations contribute. The ones with an odd number of carbon atoms have the electron configuration π^4 in the ground state and $X^1\Sigma_g^+$ symmetry. The $\pi^*-\pi$ excitation corresponds to the $^1\Sigma_u^+ - X^1\Sigma_g^+$ electronic transition.

5 Polyacetylene chains

Polyacetylene cations can be readily produced in a hot cathode source with acetylene or diacetylene as precursor. It is then merely a matter of mass-selecting the appropriate HC_nH^+ species and codepositing them with neon. The electronic spectrum of the cation kept under isolated conditions can subsequently be measured. This has so far been carried out for the ion chains with $n = 4-16$.¹⁶ The spectra of the species with an even number of carbon atoms are shown in Fig. 2.

The polyacetylene cations are open-shell species with $^2\Pi$ ground state. The transitions observed are of $^2\Pi-X^2\Pi$ symmetry and shift monotonically to the red with increasing number of carbon atoms. This is evident from Fig. 3; the energy of the transition is inversely proportional to the length of the species. This trend can be easily modelled by a particle in a 1D box where the π electrons are excited. Such an approach also predicts that the oscillator strength of the transition correlates linearly with the number of carbon atoms. This feature is a factor of why the spectra of the longer chains can be detected, even though the attainable current for the mass-selected ion is decreasing.

These electronic transitions of the polyacetylene cations HC_nH^+ with $n = 4, 6, 8$ have in fact been detected in the gas-phase as their emission spectra.¹⁷ They are shifted to higher energies in the gas phase relative to the neon matrix by 79, 135 and 143 cm^{-1} , respectively. On the basis of these trends, and the observations in the neon environment, the region for the search of these transitions in the gas-phase for the larger species is predicted sufficiently well to make this feasible.

The electronic absorption spectra of the neutral polyacetylenes, HC_nH can be obtained by codeposition of their cationic counterparts with neon, but under conditions such that neutralization is enhanced. This can be achieved by irradiation

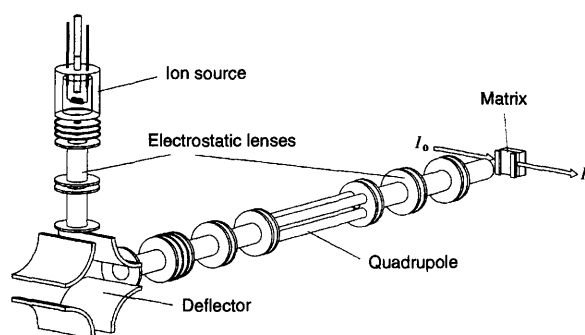


Fig. 1 Schematic arrangement of the instrument combining mass and matrix isolation spectroscopies. Mass-selected ions produced in a hot-cathode or caesium sputter source are codeposited with excess of neon to form a matrix at 5 K, and the absorption spectrum is measured by a waveguide technique.

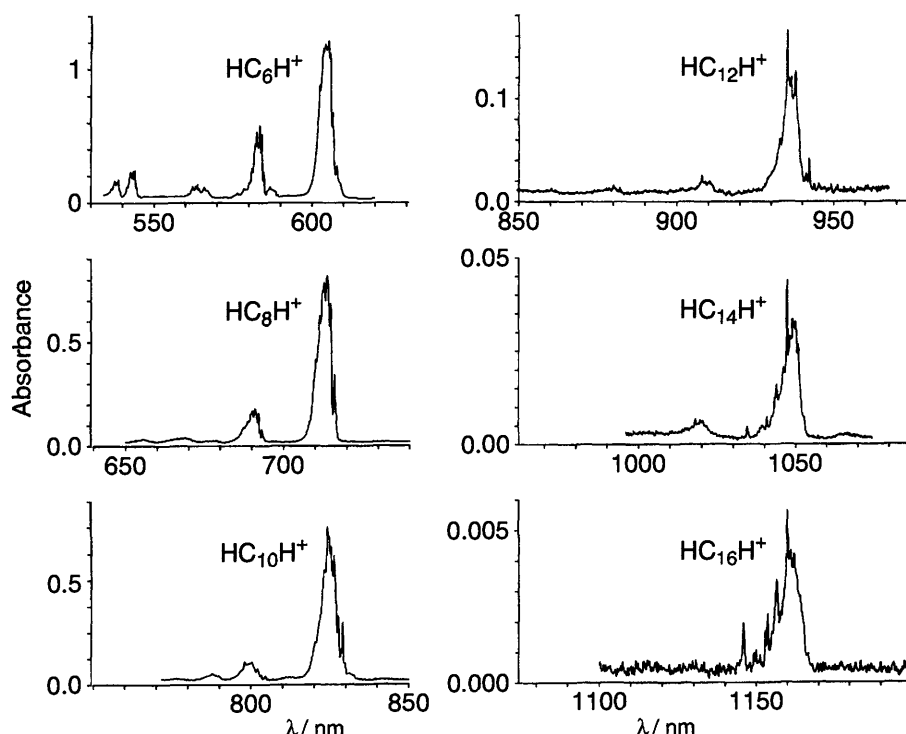


Fig. 2 The $^2\Pi-X^2\Pi$ electronic transitions of the polyacetylene cations detected as absorption spectra in neon matrices after mass-selection

of the matrix after deposition with broadband UV radiation. This photodetaches electrons from the anions present in the matrix which then recombine with the cations. By this means spectroscopy on mass-selected neutral species can be carried out.

In Fig. 4 are shown some of the recorded absorption spectra for HC_nH $n = \text{odd}$.¹⁸ The electron excitation is $\pi\text{-}\pi$ type again;

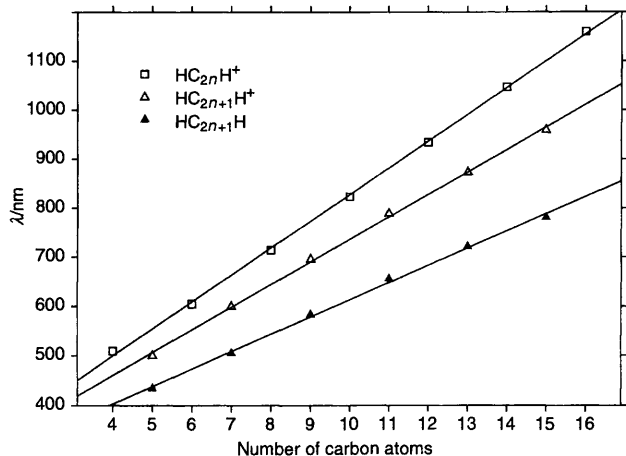


Fig. 3 The wavelength of the origin band of the $\pi\text{-}\pi$ electronic transition of the polyynes shows an approximate linear dependence on the number of carbon atoms in the chain

specifically the transitions observed are of ${}^3\Sigma_u^- \text{-} X^3\Sigma_g^-$ symmetry. The same trend as for the cations manifests itself — an approximate linear dependence of the wavelength of the transition on the number of carbon atoms. This is shown as one of the plots in Fig. 3.

The polyacetylenes with an even number of carbon atoms, HC_{2n}H , show corresponding absorption in the UV part of the spectrum. These have been measured previously in the gas phase, for $n = 2\text{-}5$, using a standard absorption approach,¹⁹ and also for the ones with n up to 10 in solution.²⁰

6 Carbon anion chains

To apply the mass-selected approach to characterize the electronic transitions of the bare carbon chains and their ions, it proved necessary to implement a different ion source. This is a caesium sputter source, which produces copious amounts of carbon anions. Caesium cations are accelerated towards a graphite rod and the resulting carbon anions are extracted. In Fig. 5 is shown the observed mass pattern; species up to C_{12}^- are produced with sufficient current for the measurement of the absorption spectrum to be possible.

Consider C_6^- as an example. After the matrix is formed the spectrum included in Fig. 6, with origin near 600 nm, is observed.¹⁴ It is readily confirmed that this spectrum is of an anion by photobleaching experiments, and that it is a member of an homologous series, because similar spectra, but red-shifted by regular increments, are observed for the successively larger

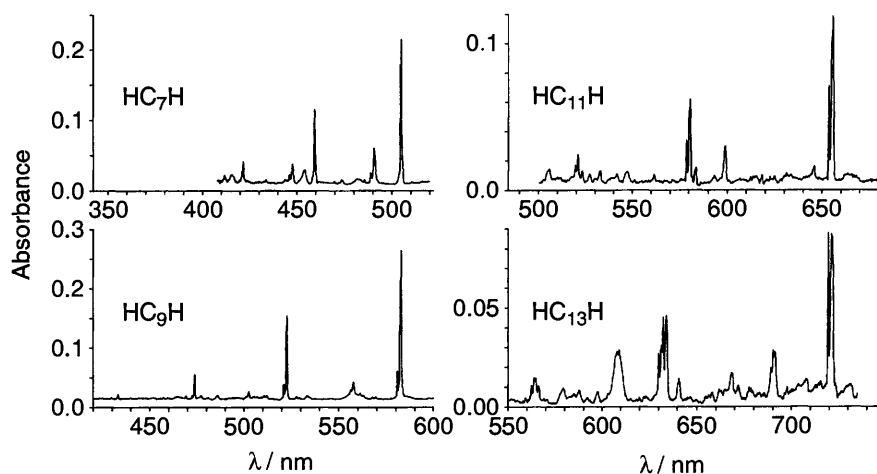


Fig. 4 Absorption spectra of the $\pi\text{-}\pi$ electronic transition (${}^3\Sigma_u^- \text{-} X^3\Sigma_g^-$ symmetry) of the HC_{2n+1}H molecules in neon matrices. These were grown using a mass-selection of the corresponding cations and subsequent UV irradiation.

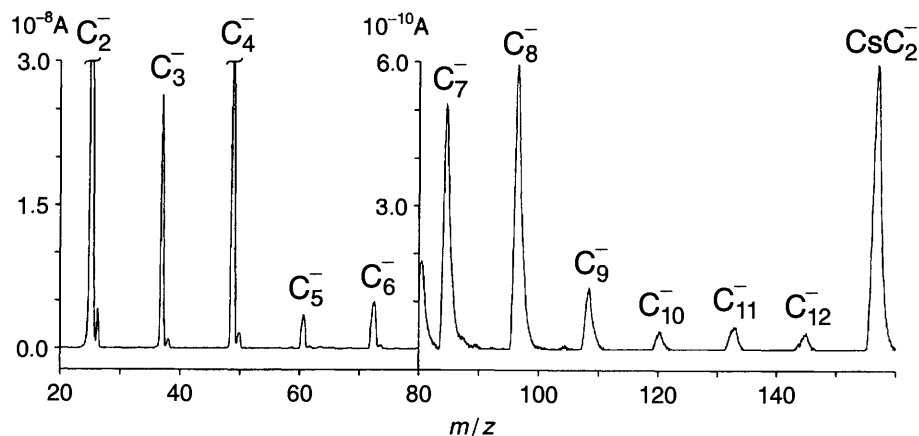


Fig. 5 Mass spectrum of the carbon anions produced using a caesium sputter source. A particular species is mass-selected and codeposited with excess of neon for the spectral measurement. The neutral chains are observed when the matrix is irradiated during or after deposition with UV light, photodetaching the electrons from the anions.

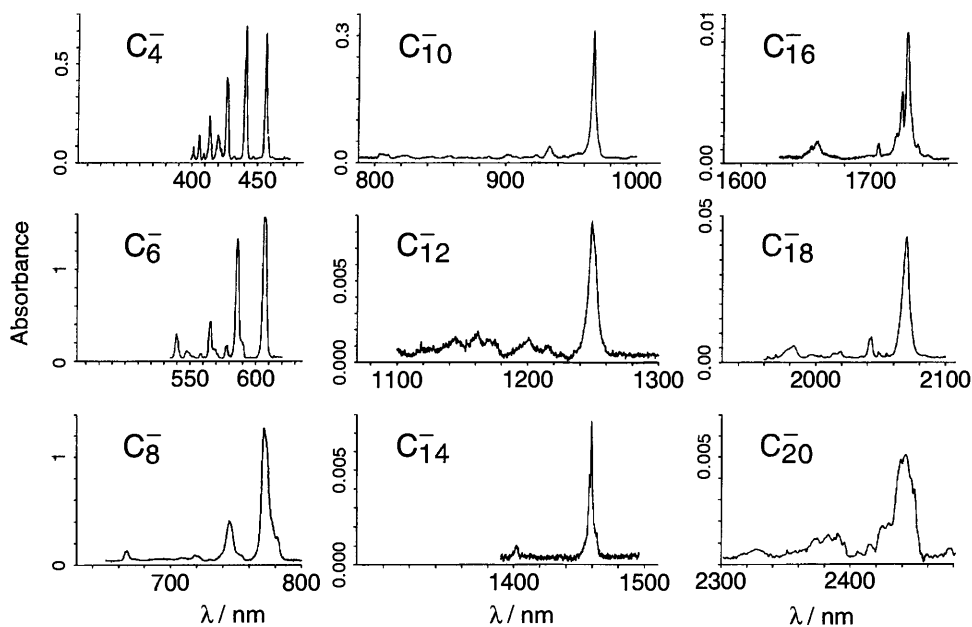


Fig. 6 The ${}^2\Pi-X^2\Pi$ electronic transitions of carbon anions measured in absorption in neon matrices

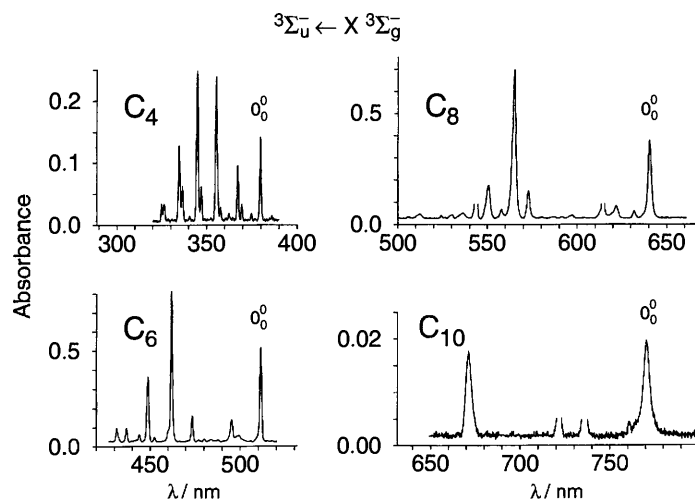


Fig. 7 The ${}^3\Sigma_u^- - X^3\Sigma_g^-$ absorption spectra of mass-selected carbon chains C_n ($n = \text{even}$) in neon matrices

species.¹¹ The nature of the transition is also clear; C_6^- is isoelectronic with HC_6H^+ , and thus it is of ${}^2\Pi-X^2\Pi$ symmetry. The Franck–Condon profile and vibrational pattern of these two ions is similar (*cf.* spectrum of HC_6H^+ in Fig. 2). Also the vibrational frequencies of the corresponding modes are comparable: HC_6H^+ : $\nu_2 = 2053$, $\nu_3 = 1880$, $\nu_4 = 617$; C_6^- : $\nu_1 = 2064$, $\nu_2 = 1817$, $\nu_3 = 607 \text{ cm}^{-1}$. The ${}^2\Pi-X^2\Pi$ transitions of the even-numbered carbon anions up to C_{20}^- have been observed.

7 Neutral carbon chains

The C_n chains with $n = \text{even}$ have ${}^3\Sigma_g^-$ ground state symmetry, whereas those with $n = \text{odd}$ have a ${}^1\Sigma_g^+$ closed-shell configuration. The IR spectra of most of the $n = 4$ –13 linear species have been obtained in the gas phase.⁵ However, their electronic transitions have not been identified, though the few articles reporting the absorption spectra of carbon vapour condensed in rare gas matrices have made suggestions on the assignment of bands to specifically sized carbon species.^{4,6} The main support for this has come from correlation of intensities of electronic and IR bands.⁷ Using the mass-selected approach, we

have been able to identify the strong transitions, ${}^3\Sigma_u^- - X^3\Sigma_g^-$ ($n = \text{even}$)¹¹ and ${}^1\Sigma_u^+ - X^1\Sigma_g^+$ ($n = \text{odd}$)²¹ for the C_n chains.

The spectrum of a specific neutral carbon chain is obtained by codeposition of the corresponding C_n^- anion with excess of neon to grow the matrix at 5 K, with concomitant irradiation with broad band UV light. The photobleaching can also be achieved after deposition; in both cases the identified electronic transition of the carbon anion disappears while a new band system appears. By this means, the ${}^3\Sigma_u^- - X^3\Sigma_g^-$ band systems for C_n $n = 4, 6, 8, 10$ have been observed as can be seen in Fig. 7. The assignment is based on (1) mass-selection, (2) photobleaching behaviour, (3) trend within an homologous series (Fig. 8), and (4) in the case of the smaller species, C_4 and C_6 , by comparison with high level *ab initio* calculations. It is interesting to note, that it has not proved possible to detect the corresponding transitions for species larger than C_{10} . The initially reported spectra¹¹ of C_{10} , C_{12} and C_{14} have turned out to be the transitions to higher electronic states of their anions; the C_{10} system has now been detected and is the one included in Fig. 7. This may be taken as an indication that the cyclic forms dominate for the neutral species of these sizes, in accord with the conclusions drawn from ion mobility measures.²¹ Pre-

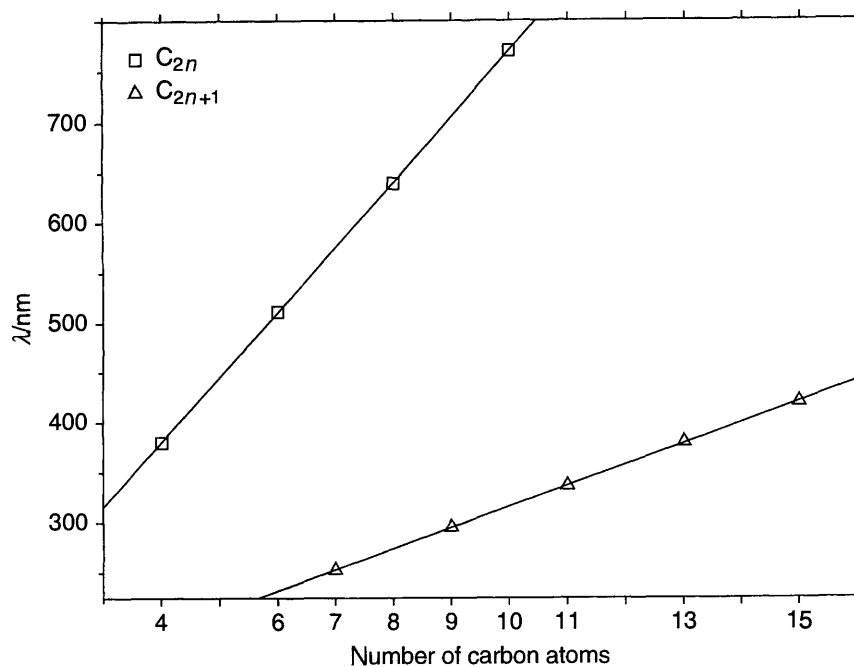


Fig. 8 Dependence of the origin band wavelength of the π - π electronic transition of the bare carbon chains C_n ($n = \text{even}: {}^3\Sigma_u^- - X^3\Sigma_g^-$; $n = \text{odd}: {}^1\Sigma_u^+ - X^1\Sigma_g^+$) on the number of carbon atoms

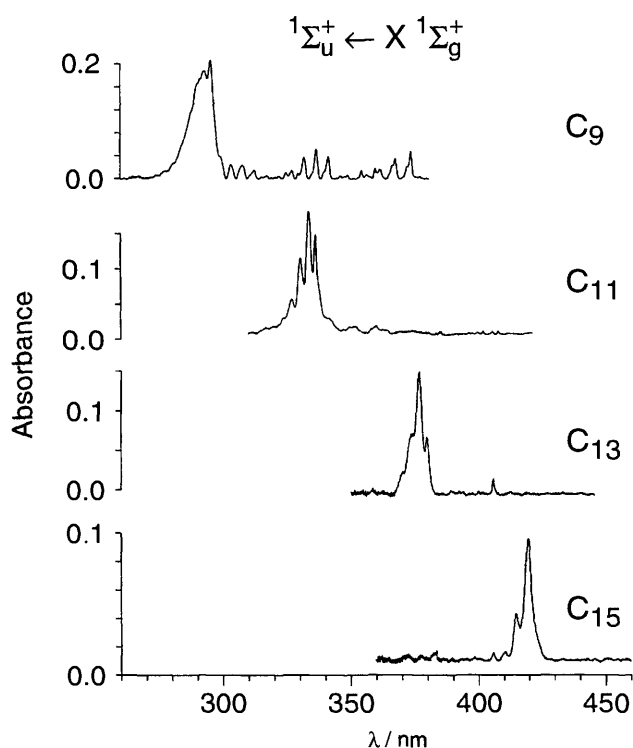


Fig. 9 Absorption spectra of the carbon chains, ${}^1\Sigma_u^+ - X^1\Sigma_g^+$ electronic transition, in neon matrices using mass-selection. The weaker structure above 300 nm in the spectrum of C_9 is due to a forbidden transition.

sumably, the sensitivity of the mass-selected approach is not yet sufficient to detect the weaker electronic transitions of the cyclic isomers.

On the other hand, the ${}^1\Sigma_u^+ - X^1\Sigma_g^+$ transition of the odd-numbered carbon chains could be detected up to $n = 15$.²² These band systems for the longer species are shown in Fig. 9. A plot of wavelength vs. length of chain dependence is shown in Fig. 8, an extrapolation of which yields a prediction for the hitherto unmeasured longer species. Furthermore, the trend on the high energy size predicts that the yet to be observed

${}^1\Sigma_u^+ - X^1\Sigma_g^+$ transition of C_3 should be located near 170 nm. The well-known Comet band system of C_3 , $A^1\Pi_u - X^1\Sigma_g^+$, lies near 300 nm, and the corresponding transitions of C_5 and C_7 are also discernible in the matrix near 510 and 542 nm, respectively.²²

8 Monohydrogenated carbon chains

The electronic spectra of the $C_{2n}H$ chains, with $n = 3-8$, have also been detected by mass-selection of $C_{2n}H^-$ anions, and photodetachment during growth of the matrix.¹¹ The hot-cathode anion source with diacetylene as input proved expedient for the $C_{2n}H^-$ production.

The $C_{2n}H$ chains are isoelectronic with the C_{2n}^- and $HC_{2n}H^+$ ions, and accordingly show the strong ${}^2\Pi - X^2\Pi$ transition in a similar wavelength region. Furthermore, the discernible vibrational frequencies for such isoelectronic species are similar as is the overall Franck-Condon shape of the band systems. The corresponding transitions of the chains with odd-number of carbon atoms, $C_{2n+1}H$ have not yet been obtained.

9 Nitrogen containing chains

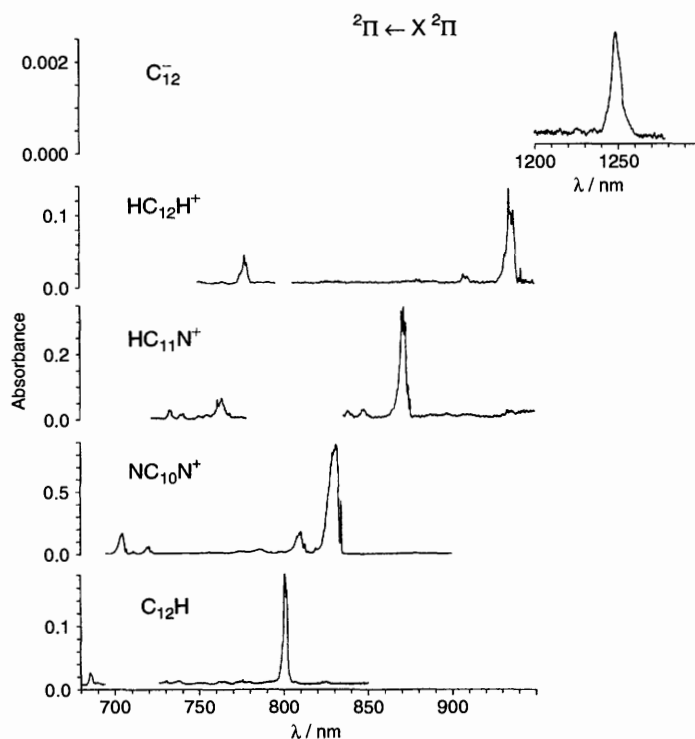
It proved possible to measure and assign the ${}^2\Pi - X^2\Pi$ electronic transitions of cyanopolyacetylene cations HC_nCN^+ ($n = 4-12$) and NCC_nCN^+ ($n = 2-10$).²³ This was carried out using a hot-cathode discharge source for the cation production with cyanoacetylene or dicyanoacetylene as precursor gas. The same pattern as for the carbon chains is manifested for these homologous series. Because the HC_nCN^+ , NC_nN^+ , $C_{n+2}H$ and $HC_{n+2}H^+$ species are isoelectronic, the series can be directly compared and they indeed show the ${}^2\Pi - X^2\Pi$ band systems in a similar region. This can be seen by comparison of the spectra of C_{12}^- , $C_{12}H$, $HC_{12}H^+$, $HC_{11}N^+$ and $NC_{10}N^+$ in Fig. 10; the origin bands lie within a 0.6 eV span. Table 1 shows the wavelengths of the observed origin bands of the electronic transitions of the carbon chains identified hitherto in neon matrices using the mass-selected approach.

10 Gas-phase studies

Because it has always been the aim to use the matrix observations as a basis for gas-phase studies of the carbon chains, it is useful to consider the data for the species where this

Table 1 Wavelength (λ/nm) of the origin band of the characteristic $\pi\text{-}\pi$ transition of carbon chains observed in neon matrices

$C_{2n+1}: {}^1\Sigma_u^+ \leftarrow X {}^1\Sigma_g^+$	$C_{2n}^-: {}^2\Pi \leftarrow X {}^2\Pi$	$C_{2n}: {}^3\Sigma_u^- \leftarrow X {}^3\Sigma_g^-$
C_7 253	C_4^- 457	C_4 380
C_9 295	C_6^- 608	C_6 511
C_{11} 336	C_8^- 773	C_8 640
C_{13} 380	C_{10}^- 967	C_{10} 735
C_{15} 420	C_{12}^- 1249	
	C_{14}^- 1460	
	C_{16}^- 1729	
	C_{18}^- 2069	
	C_{20}^- 2440	
$HC_{2n+1}H: {}^3\Sigma_u^- \leftarrow X {}^3\Sigma_g^-$	$C_{2n}H: {}^2\Pi \leftarrow X {}^2\Pi$	$HC_{2n}N^+: {}^2\Pi \leftarrow X {}^2\Pi$
HC_5H 434	C_6H 530	HC_6N^+ 570
HC_7H 505	C_8H 631	HC_8N^+ 657
HC_9H 582	$C_{10}H$ 722	$HC_{10}N^+$ 747
$HC_{11}H$ 655	$C_{12}H$ 801	$HC_{12}N^+$ 832
$HC_{13}H$ 721	$C_{14}H$ 866	
$HC_{15}H$ 781	$C_{16}H$ 924	
$HC_{2n+1}N^+: {}^2\Pi \leftarrow X {}^2\Pi$	$NC_{2n}N^+: {}^2\Pi \leftarrow X {}^2\Pi$	$NC_{2n+1}N^+: {}^2\Pi \leftarrow X {}^2\Pi$
HC_5N^+ 584	NC_4N^+ 598	NC_7N^+ 629
HC_7N^+ 674	NC_6N^+ 659	NC_9N^+ 713
HC_9N^+ 771	NC_8N^+ 741	$NC_{11}N^+$ 795
$HC_{11}N^+$ 871	$NC_{10}N^+$ 831	
$HC_{13}N^+$ 973	$NC_{12}N^+$ 923	
$HC_{2n}H^+: {}^2\Pi_u \leftarrow X {}^2\Pi_g$	$HC_{2n+1}H^+: {}^2\Pi \leftarrow X {}^2\Pi$	
HC_4H^+ 509	HC_5H^+ 499	
HC_6H^+ 605	HC_7H^+ 600	
HC_8H^+ 713	HC_9H^+ 659	
$HC_{10}H^+$ 823	$HC_{11}H^+$ 789	
$HC_{12}H^+$ 934	$HC_{13}H^+$ 873	
$HC_{14}H^+$ 1047	$HC_{15}H^+$ 959	
$HC_{16}H^+$ 1160		

**Fig. 10** The ${}^2\Pi\text{-}X^2\Pi$ electronic absorption spectra of isoelectronic carbon chains in neon matrices

has already proved possible. Also relevant is a comparison of the gas–neon matrix shifts and apparent trends.

Prior to the study of the electronic spectra of mass-selected carbon chains and their ions in neon matrices, the ${}^2\Pi\text{-}X^2\Pi$ transitions of cations of three polyacetylenes, HC_nH^+ $n = 4, 6, 8$, and of three cyanopolyacetylenes, HC_5N^+ , NC_nN^+ $n = 4, 6$, were observed in the gas-phase by emission spectroscopy.²⁴

Recently, the ${}^2\Pi\text{-}X^2\Pi$ transitions could be detected in the gas-phase for the three carbon anions C_n^- $n = 4, 6, 8$ using a two-colour photodetachment approach.¹⁰ The latter experiments could be carried out because the location of the transitions was known from the matrix studies.¹¹ The ${}^2\Pi\text{-}X^2\Pi$ band system of C_6H could for the same reason be observed in a discharge by a sensitive laser absorption technique ('cavity ring-down').²⁵

Table 2 Gas–neon matrix shifts of the origin bands of the ${}^2\Pi \leftarrow X\ ^2\Pi$ electronic transitions of carbon chains. All values in cm^{-1} .

Species	ν_{0-0}		Shift	Ref.
	Gas	Neon		
HC_4H^+	19724	19645	79	16, 17
HC_6H^+	16670	16535	135	16, 17
HC_8H^+	14160	14017	143	16, 17
HC_5H^+	17190	17130	60	23, 24
NC_4N^+	16781	16719	62	23, 24
NC_6N^+	15260	15173	87	23, 24
C_6H	18996	18854	142	11, 25
C_4^-	21872	21896	-24	10, 11
C_6^-	16476	16458	18	10, 11
C_8^-	12963	12933	30	10, 11

In Table 2 is given a comparison of the gas and matrix frequencies of the origin bands of the electronic transitions of these carbon chains. It can be seen that the shift increases with size of the molecule; in the gas-phase the transitions are found to higher energies (with the exception of C_4^-). The anions show rather modest shifts, and it appears that cations and neutrals which have about the same lengths show similar displacements: HC_6H^+ ($135\ \text{cm}^{-1}$), C_6H ($142\ \text{cm}^{-1}$). On the other hand, the isoelectronic cyanopolyacetylene cations show smaller shifts: HC_5N^+ ($60\ \text{cm}^{-1}$), NC_4N^+ ($62\ \text{cm}^{-1}$).

11 Predictions for other carbon chains

As is evident from Fig. 10, carbon chains which are isoelectronic have the corresponding electronic transitions in a similar spectral region. Therefore this information can be used to predict the absorption characteristics of the yet unstudied species. For example, the HC_n^+ , and C_{n-1}N^+ , ions are isoelectronic with the bare carbon chains, and will follow their pattern (Fig. 8). Similarly, the neutral C_{n-1}N , and HC_n , chains, will show strong π - π transitions in the same region as the isoelectronic HC_nH^+ species, whose ${}^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ band systems are located in the plots of Fig. 3 and can be extrapolated accordingly.

12 Relevance to the diffuse interstellar bands

Carbon chains are among the particularly attractive candidates as carriers of the diffuse interstellar bands (DIBs),²⁶ especially in view of the detection of carbon chains in dark clouds and carbon stars.¹ Thus it is worthwhile to relate the understanding of their electronic spectra to this problem. In fact, on the basis of the observations made on the absorption spectra of mass-selected species in neon matrices in the initial experiments, the number of coincidences (*i.e.* within a certain uncertainty taken to be representative of the gas–matrix shift) between the absorption bands and DIBs, indicated that the carbon chains and their monohydro derivatives are good candidates for the carriers.²⁷

One can now consider the species in more detail by combining the spectroscopic results with the astronomical observations as well as physical and chemical restrictions on the molecules. The stellar observations are that nearly two hundred absorption features are attributed to DIBs.²⁸ These are found in the 400–900 nm region, though a few absorptions below and in the near IR have also been so interpreted. Thus from the observed trends among the carbon chains studied, whereby the strong π - π transition shifts by a particular increment to the red as the number of carbon atoms increases (Figs. 3,8), the length of the chain necessary for the molecule to absorb in the DIB window can be determined from the plots. Analogously, this can be predicted for the hitherto unmeasured, but isoelectronic, or structurally similar chains, also those including nitrogen or oxygen atoms. The series of carbon chains likely to be easily

formed in the diffuse clouds are: C_n , C_nH , HC_nH (or their H_2C_n isomers) and their ions, as well as the related N- and O-containing species.

The astrophysical conditions dictate that the species have to be large enough to be stable with respect to photodissociation to starlight penetrating the diffuse clouds, or that efficient syntheses are operative.²⁹ Thus a sufficient size has been considered to be molecules with say > 10 – 15 atoms.³⁰ If this criterion is applied, then a number of the smaller carbon chains that would absorb in the 400–900 nm spectral window can be eliminated.

Examples of this are the bare carbon chains with even number of atoms. As is seen in Fig. 8, C_n $n = 6, 8, 10$ would absorb in the DIB region but are deemed as too small to be photostable. On the other hand the odd-numbered carbon chains, C_n $n = 15$ – 37 will show their strong π - π transition in the 400–900 nm gap and are large enough. However, it has been shown both experimentally and theoretically, that carbon species comprising more than 20 atoms prefer a ring structure,²¹ which may be the chemical restriction on the length of the chains to be considered.

These arguments lead to a natural restriction on the number of possible species, which is attractive because there appear to be a limited number of stronger DIBs. The chains which would satisfy the above discussed criteria are then the odd carbon chains C_{2n+1} , and their isoelectronic analogues HC_{2n+1}^+ and C_{2n}N^+ , with $n > 9$ but perhaps terminating in the mid-twenties. Not specifically discussed, but chains which will have similar spectral characteristics and need to be considered are the oxygen-containing ones, C_nO , and the cumulene type structures H_2C_n , $\text{H}_2\text{C}_n\text{O}$. As an example, the C_nO species with $n = \text{odd}$ have ${}^1\Sigma_g^+$ ground state, whereas those with $n = \text{even}$ ${}^3\Sigma_g^-$, and will behave spectroscopically like the odd- or even-numbered C_n chains, respectively (*cf.* Fig. 8). It is relevant to note that H_2C_n , C_nH and C_nO type chains have been detected in dark clouds by radioastronomy.³¹

13 Outlook

The observation of the electronic spectra of a number of homologous series of the carbon chains in neon matrices by utilising mass-selection, has given the breakthrough in providing the location of the transitions so that gas-phase studies are a realistic proposition, as well as for astrophysical considerations. The interesting chains still to be characterized by this technique are the species containing oxygen and the cumulenes.

In connection with the DIBs assignment, the data define on which type of carbon chains interest should be focused. The next stage is then a concerted effort at obtaining the electronic spectra of the relevant species in the gas-phase. To this end a variety of laser-based approaches are envisaged. In the case of the anions the two-colour laser photodetachment approach has already proven to be successful for the smaller species;¹⁰ for the neutrals laser absorption methods, such as used for C_6H detection,²⁵ and resonant photon ionization approaches are likely to succeed because the wavelength region of the electronic transitions is known in neon matrices.

14 Acknowledgements

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