Electronic spectroscopy of carbon chains and relevance to astrophysics

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Laboratory measurements of electronic transitions in carbon chains are presented. Guided by the results found in neon matrices, gas-phase spectra have been obtained with two different experimental approaches. Electronic transitions of neutral carbon chains are detected in a supersonic slit jet plasma by cavity ring-down (CRD) spectroscopy, and those of mass-selected anions are probed by resonant two-colour electron photodetachment. The successful combination of matrix and gas-phase experiments is demonstrated for the examples of C_6H and $C_{14}H^-$. These, and other previous measurements on electronic transitions of long carbon chains in the gas phase, are compared with the tabulated wavelengths of the diffuse interstellar bands. In the case of the $A\,^2\Pi_u$–$X\,^2\Pi_g$ transition of C_7^- the origin and three intense bands in the gas-phase spectrum match, within ± 0.2 nm error limits, diffuse interstellar bands which have comparable FWHMs and equivalent widths.

Carbon chains are considered among the attractive candidates as carriers of some of the diffuse interstellar bands (DIBs).[1] Following the initial suggestion and arguments by Douglas,[2] this concept has received further encouragement, on one hand by the actual detection of molecules with a carbon-chain skeleton in dense interstellar clouds by microwave spectroscopy[3] and on the other by understanding the spectral properties of the characteristic π–π electronic transitions.[4] The latter has come about following the detection of such spectra in absorption for a number of homologous series using the technique which combines mass-selection with matrix isolation.[5] Thus, to answer questions as to which types and sizes of carbon chains, their ions and simple derivatives with H, N and O need to be spectroscopically characterized in the gas phase, the following strategy has been pursued.

The initial step is the observation and identification of the vibronic spectra of the species under study in neon matrices. With this information in hand, the planning of gas-phase experiments becomes a realistic proposition. In fact the gas-phase results reported in this article, as well as those in recent publications on carbon anions,[6] substantiate this philosophy. Independent of such measurements, the patterns in the spectroscopic signatures of carbon chains can then be considered together with astrophysical constraints, as well as chemical ones, to decide which types and sizes should be measured in the gas phase. Clearly, the systematic detection of the electronic spectra in the gas phase for numerous species, as has proven possible in neon matrices, is currently not trivial.

The dependence of the electronic spectra of carbon chains in neon matrices on the size of the system has led to the conclusion that species such as C_{2n+1} ($n = 8$–18 or so), and their isoelectronic analogues, would have their strong π–π electronic transitions in

the 400–900 nm wavelength range,[4] where diffuse interstellar absorptions are mainly observed.[7] In this article, the emphasis is placed on the observation of the gas-phase electronic transitions of a few species which, however, from size and stability considerations alone would not necessarily be *a priori* the ones selected for comparison with astrophysical data. Rather, owing to the difficulties of gas-phase studies, these should be regarded as pilot approaches to show that such measurements have now become feasible. In particular, this has led to the first observation of electronic spectra of neutral carbon chains, C_nH, and of the largest species to date, $C_{14}H^-$, in the gas phase.

Two different experimental strategies are considered: (1) the detection of neutral carbon chains in absorption by using cavity ring-down (CRD) spectroscopy in a supersonic slit jet expansion plasma and (2) resonant two-colour electron photodetachment of mass-selected anions. In both cases, the observation of electronic transitions in a neon matrix was the starting point. In the final section selected gas-phase data on electronic transitions of carbon chains and their ions are directly compared with the catalogue of DIBs.[7]

Gas-phase electronic spectrum of C_6H

The $^2\Pi \leftarrow X\,^2\Pi$ electronic absorption spectrum of C_6H was initially identified in a 5 K neon matrix using the mass-selective technique.[5] Based on this information, this transition was detected in the gas phase by means of CRD spectroscopy in a hollow cathode discharge cell.[8] The approach has now undergone further development, increasing the sensitivity of the measurement by using a plasma generated in a supersonic slit jet expansion.

Experimental

CRD spectroscopy has proven in recent years to be a powerful technique for direct absorption spectroscopy. The intrinsic insensitivity to light-source fluctuations and the very long absorption lengths make it ideally suited for the study of weak molecular transitions, or of molecules that are difficult to generate in large abundance. Since its introduction as a spectroscopic tool in 1988,[9] it has been applied in different fields: trace-gas detection, combustion, discharges and molecular beams.[10,11] Molecular ions could also be detected in a pulsed hollow-cathode discharge,[12] leading to estimated detection limits of around 10^7 molecules cm^{-3}. This set-up was the one used to detect the $^2\Pi–X\,^2\Pi$ electronic transition of C_6H.[8] Here, the extension of this approach is presented, whereby the hollow cathode has been replaced by a supersonic expansion plasma.

In the last few years much effort has been put into the development of techniques that combine the advantages of a two-dimensional supersonic expansion through a small slit (high densities, adiabatic cooling and complexation) and plasma generation (ion and radical production). Direct absorption spectra of several rotationally cold molecular ions, radicals and an ionic complex have been reported, using production techniques ranging from ablation,[13] photolysis[14] and discharge,[15] to electron impact ionization.[16] Impressive have been the observations of rotationally resolved IR spectra of carbon chains, C_n, $n \leqslant 13$, following excimer laser ablation of a carbon rod positioned in the throat of the slit.[17]

The current experimental set-up consists of a standard CRD unit sampling a supersonic slit jet (Fig. 1). The latter is located in a large stainless-steel cross-piece evacuated by a Roots blower. The mirror housings are connected with flexible bellows to the opposite sides of the cross-piece. Two anti-reflection coated quartz windows are fixed outside the cavity and seal the chamber. The deposition of contaminants on the mirrors is restricted by a curtain of helium. The nozzle is mounted in the centre of the chamber
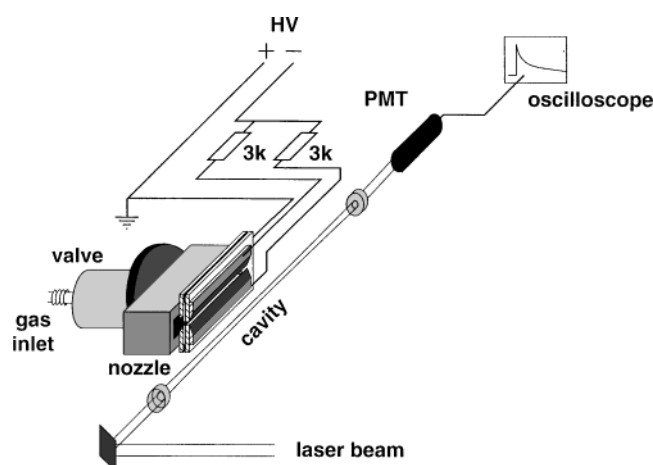
Fig. 1 Schematic of the experimental set-up for the measurement of electronic absorption spectra of neutral carbon chains by CRD spectroscopy

with its slit parallel to the laser beam. The distance of the orifice to the optical axis can be varied from 1 to 15 mm. The gas (0.2 to 1% C_2H_2 or C_2D_2 in helium, 5 bar backing pressure) is expanded through a 3 cm × 250 μm pulsed slit (Fig. 1). The pressure in the chamber during operation is around 150 mTorr.

The orifice of the slit comprises an insulator, metal plate, second insulator and two sharp jaws to which a pulsed negative voltage of 800–1200 V (50 mA, 100 μs) is applied. The inner metal plate is grounded while the body floats. This configuration leads to a discharge over the total length of the slit. Furthermore, carbon dust is not produced inside the slit and thus the discharge is stable for many hours.

Although the volume in the slit has been kept small, the effective gas pulse has a small delay and smears out the valve's nominal opening from 350 to typically 500–750 μs. The whole experiment runs at 30 Hz; a master signal is sent to a delay generator, from which the excimer laser, gas valve and discharge are independently triggered. With typical ring-down times of 40 μs effective absorption lengths of *ca.* 1 km are achieved.

$^2\Pi$–X $^2\Pi$ Electronic transition of C_6H

The initial observation of the $^2\Pi$–X $^2\Pi$ transition in the gas phase was in a hollow-cathode discharge.[8] The resulting spectrum ($T_{rot} \approx 350$ K) reveals only the unresolved R-branches of the two spin–orbit components, $^2\Pi_{1/2}$–X $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$–X $^2\Pi_{3/2}$ [Fig. 2(a)]. Consequently, it was possible to determine neither accurate rotational constants nor the spin–orbit constant A' for the excited state. In contrast, the ground electronic state parameters are well characterized from the microwave spectrum of C_6H.[18] Fig. 2(b) shows a low-resolution (0.1 cm^{-1} laser bandwidth) spectrum in the region of the origin band of the $^2\Pi$–X $^2\Pi$ electronic transition of C_6H recorded in the slit jet expansion. The rotational temperature is *ca.* 45 K. The P and R branches of both spin–orbit components are visible, as well as the Q-branch of the $^2\Pi_{3/2}$–X $^2\Pi_{3/2}$ sub-band. This is because of the more favourable Hönl–London factors compared to the $\Omega = 1/2$ system. Furthermore, at $T_{rot} = 45$ K, the population density for the $\Omega = 3/2$ component is *ca.* 30% higher than for $\Omega = 1/2$; the ground state spin–orbit splitting is *ca.* −15 cm^{-1}. The Q-branches are not observed in the warm spectrum [Fig. 2(a)] due to the population distribution being over many rotational levels. The Q-heads of the origin bands for the $\Omega = 3/2$ and 1/2 components are observed and estimated at 18 985.5(2) and
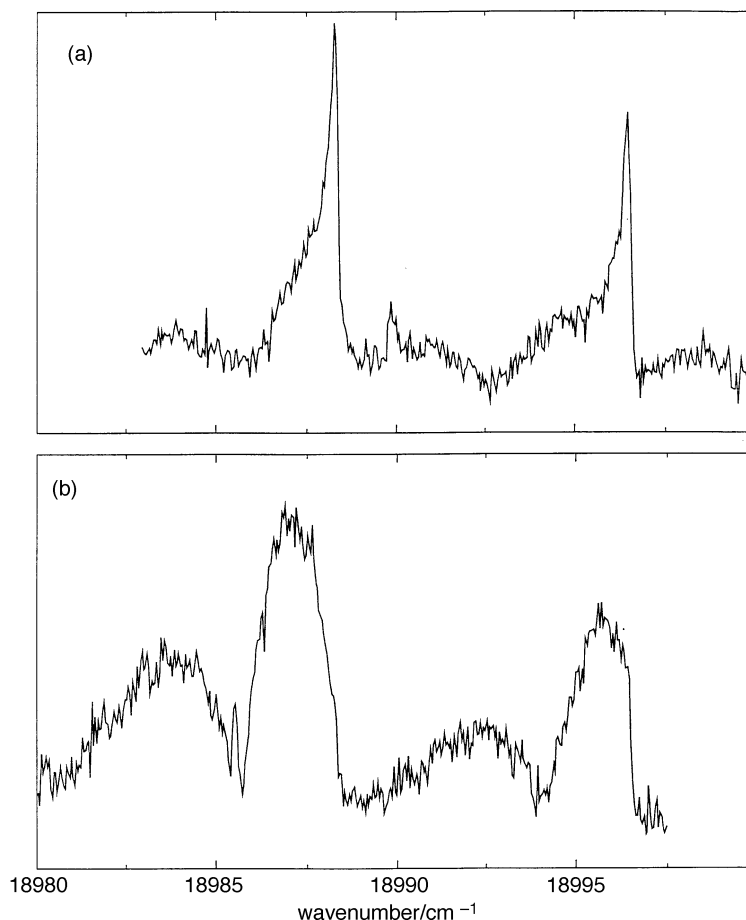
Fig. 2 (a) Spectrum of the origin band of the $^2\Pi$–X$^2\Pi$ transition of C_6H measured in a hollow-cathode discharge at 350 K. The two heads are in the R-branches of the $\Omega = 3/2$ and 1/2 components. (b) Spectrum at $T_{rot} = 45$ K, measured in a supersonic slit nozzle plasma. P and R branches are visible as well as the Q-branch of the $^2\Pi_{3/2}$–X$^2\Pi_{3/2}$ band.

18 994.7(4) cm^{-1}, respectively. In the spectrum of C_6D the origin bands are shifted by 51.3 cm^{-1} to higher energies compared with C_6H.

An upper-state spin–orbit constant $A' = -23.5(2)$ cm^{-1} is obtained, assuming a ground-state value $A'' = -15.09$ cm^{-1}, determined from the microwave spectrum.[18] In the analysis of the spectrum in the hollow-cathode discharge,[8] only $|A'-A''|$ could be deduced because the Q-branches were not discernible, and it was assumed that $A' < A''$. However, the spectrum in Fig. 2 reveals clearly that $A' > A''$. Consequently, the blue shift of the origin band ($\Omega = 3/2$ component) in the gas phase, relative to its position in the neon matrix, is 131 cm^{-1}, rather than the 142 cm^{-1} value quoted previously.[8] This shift can be compared with the gas–neon matrix shift of 122 cm^{-1} observed for the $^2\Pi$–X$^2\Pi$ transition of the isoelectronic triacetylene cation.[4]

The spectral measurements in the slit nozzle are nearly Doppler free and thus the rotational structure of the transition could be resolved. With an intracavity etalon a laser bandwidth of 0.04 cm^{-1} can be achieved, which is comparable with the rotational constant of C_6H. Fig. 3 presents the rotationally resolved origin band of the $^2\Pi_{3/2}$–X$^2\Pi_{3/2}$ component. A standard $^2\Pi$–X$^2\Pi$ Hamiltonian was used to fit more than
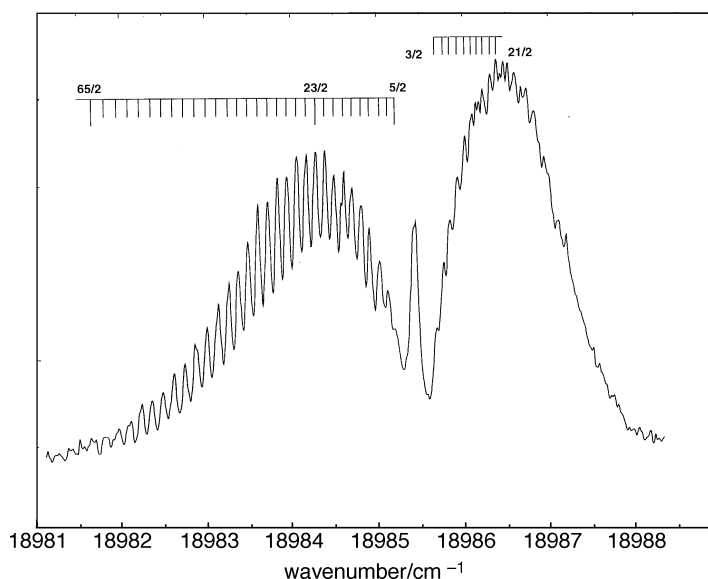
Fig. 3 Rotational structure of the origin band in the $^2\Pi_{3/2}$–X$^2\Pi_{3/2}$ electronic transition of C_6H measured by CRD spectroscopy in a slit nozzle plasma

30 observed transitions in the $\Omega = 3/2$ system, mainly occurring in the P-branch. In the fit, the accurate set of spectroscopic constants inferred from the microwave spectrum was used for the ground electronic state. The upper-state rotational constant is determined as $B' = 0.045\,563(23)$ cm^{-1}, where D' has been kept fixed to the ground-state value. In the case of the $\Omega = 1/2$ system the lower signal-to-noise ratio precluded the accurate measurement of the line positions.

This technique has now also been applied successfully to detect the corresponding $^2\Pi$–X$^2\Pi$ electronic transitions of longer members of this homologous series. The centre frequencies of the unresolved origin bands of C_8H and $C_{10}H$ have been identified at $15\,973.5(1.0)$ cm^{-1} and $14\,000(3)$ cm^{-1}, respectively.[19]
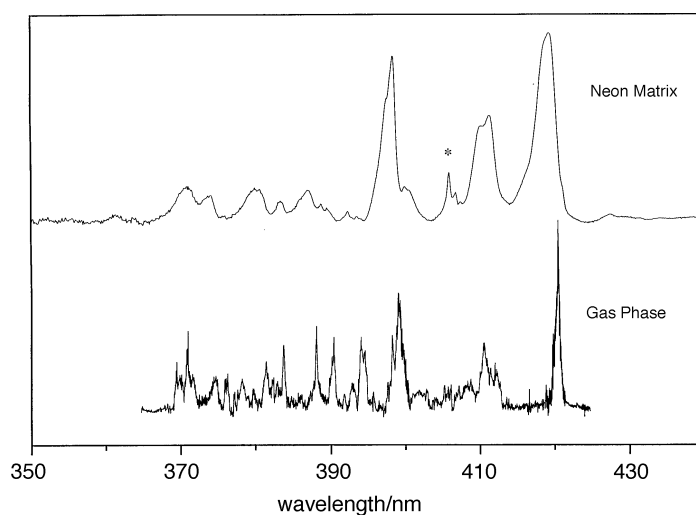
Electronic spectrum of $C_{14}H^-$

Absorption spectrum in a neon matrix

The combined technique of mass-selection with matrix isolation has been used to identify the characteristic electronic transitions of a number of homologous series of carbon chains. These include neutrals: C_{2n} ($n = 2$–5),[20] C_{2n+1} ($n = 2$–7),[21] $C_{2n}H$ ($n = 3$–8),[20] $HC_{2n+1}H$ ($n = 2$–7),[22] anions: C_n^- ($n \leqslant 20$),[23,24] and cations: HC_nH^+ ($n \leqslant 16$).[25] In the measurements described here, $C_{14}H^-$ was chosen as an example of a longer species, with the goal of detecting its electronic transitions in the gas phase. As a first step, the electronic absorption spectrum in a neon matrix was sought. A hot-cathode anion source was fed with a diacetylene–argon mixture (1 : 5), and the resulting ion beam was mass-selected and codeposited with neon at 6 K on a rhodium-coated sapphire plate.

Mainly, the species $C_{2n}H^-$ are formed for $n \leqslant 7$, whereas the larger anions contain predominantly 2 and 4 hydrogen atoms. Following the deposition of mass-selected $C_{14}H_x^-$ ions ($x = 0$–4, with 1, 2 being the strongest), the absorption spectrum was measured with the waveguide technique[26] and is shown in Fig. 4 (top). The mass-resolution

was deliberately degraded to obtain higher anion currents. When the resolution was increased to select a specific $C_{14}H_x^-$ species, the observed band system was strongest for $x = 1$. The observation that the system is also weakly present when depositions with $x = 2, 4$ are performed, can be understood in terms of fragmentation due to the high kinetic energy of the ions. The 420 nm band system can be eliminated through irradiation of the matrix with photons from a medium-pressure mercury lamp, after which the known $^2\Pi \leftarrow X\,^2\Pi$ electronic transition of neutral $C_{14}H$, with origin band at 865 nm,[20] becomes apparent.

The observed electronic absorption spectrum (Fig. 4) shows features characteristic of π–π transitions of carbon chains: a strong origin band and vibrational excitation of a number of stretching modes. As is often the case in matrices, degenerate bending modes in even quanta are probably also excited. Corresponding band systems have been observed for other members of this series $C_{2n}H^-$ ($n = 3$–9), and a plot of the wavelength of their origin bands as a function of the number of carbon atoms shows an approximately linear dependence,[27] a characteristic feature of a homologous series. Because the observed band systems of the $C_{2n}H^-$ molecules are intense, comparable with the other allowed π–π ones of carbon chains hitherto observed, it is supposed that they are due to $^1\Sigma^+ \leftarrow X\,^1\Sigma^+$ electronic transitions. These have also been observed for the isoelectronic polyacetylenes, $HC_{2n}H$, in neon matrices[27] and in solution up to $n = 12$,[28] but they lie to higher energies. For example, in the case of $HC_{14}H$, this band system is *ca.* 1.5 eV above that of $C_{14}H^-$. This difference is quite large for isoelectronic species and consequently the assignment of the band system (Fig. 4) to a forbidden $^1\Delta \leftarrow X\,^1\Sigma^+$ transition was considered. The latter band system is observed for the smaller members of the $HC_{2n}H$ series, $n = 2, 3$ in the gas phase[29] and for $n \leqslant 5$ in solution.[30] Extrapolation of these transition frequencies to $n = 7$ leads to energies close to the observed band of $C_{14}H^-$. However, the $^1\Delta \leftarrow X\,^1\Sigma^+$ band system is not observed for the longer polyacetylenes and no second, intense band system is apparent in the neon matrix spectrum of $C_{14}H^-$ at energies higher than that of the 420 nm one. Transitions above 5 eV would lie above the electron detachment threshold of $C_{14}H^-$. Thus the $^1\Sigma^+ \leftarrow X\,^1\Sigma^+$ assignment is preferred. Another explanation for the unusually large shift (*ca.* 1.5 eV) relative to

Fig. 4 Electronic transition of $C_{14}H^-$ recorded by direct absorption at 6 K in the neon matrix (top trace) and resonant two-colour electron photodetachment spectroscopy in the gas phase at $T \approx 100$ K (bottom trace). The asterisk denotes the absorption peak of C_3 formed by fragmentation.

$HC_{14}H$ may be that the electronic structure of $C_{14}H^-$ is more cumulenic than acety-lenic in character, or that the geometric structure may not be linear, *e.g.* bent or ring-chained as has been observed for similar neutral species.[3] Consequently, the nature of the observed transition in $C_{14}H^-$ cannot be definitively determined.

Electronic spectrum of $C_{14}H^-$ in the gas phase

Experimental

Based on the information on the electronic transition of $C_{14}H^-$ observed in a neon matrix, the search in the gas phase was undertaken. The $C_{14}H^-$ anions were generated in a pulsed DC gas discharge through a mixture of acetylene and argon, followed by a supersonic expansion. This produces anionic carbon species of the general form $C_nH_m^-$, which were subsequently mass-selected in a Wiley–MacLaren time-of-flight spectro-meter. The resonant two-colour electron photodetachment (R2CPD) technique was then employed to measure their electronic transitions. This approach has already been used to measure the $^2\Pi–X\,^2\Pi$ electronic transitions of linear carbon anions, C_2^-, C_4^-–C_9^-.[6,31,32]

The R2CPD approach is a pump and probe experiment in which two laser beams intersect a mass-selected anion beam. Mass selectivity is obtained by varying the delay of the laser pulses, such that they interact with only the carbon anion of choice. The two photons (hv_1 and hv_2) are generated by an excimer pumped dye and a Nd : YAG laser, respectively, with v_1 tuned over the expected wavelength range of the transition of the mass-selected ion (1). The second photon, hv_2, has sufficient energy to detach an electron from the excited species but not from the ground state (2):

$$M^- + hv_1 \rightarrow M^-* \tag{1}$$

$$M^-* + hv_2 \rightarrow M + e^- \tag{2}$$

The resultant neutral product is then detected at a multichannel-plate array. By apply-ing a retarding voltage to a grid above the detector, which delays the arrival of the anion beam with respect to the neutrals, it is possible to detect parent ions and product neutrals, thus enabling normalisation of the spectra for fluctuations in the production of parent cluster ions in the source.

Gas-phase spectrum

The R2CPD spectrum of the expected band system of $C_{14}H^-$ is shown in the lower trace of Fig. 4. There is a good correspondence between the stronger gas-phase and the neon matrix bands. The gas-phase spectrum, however, yields a greater number of spec-tral features, but those which correlate with matrix bands indicate a neon-environment-induced blue shift of 50 ± 20 cm^{-1}. It should, however, be pointed out that this shift refers to the maxima of the bands observed in the neon matrix. Owing to the width of these peaks, the shift with respect to the zero-phonon line (which is not discernible) will be less. Blue shifts on passing from the gas phase to the neon environment are unusual, being only observed for electronic transitions of a few of the smaller carbon anions, C_n^- ($n = 2, 4, 5$). For neutral and cationic carbon chains, red shifts are the rule.[4]

The positions of the band maxima are listed in Table 1, together with possible vibra-tional assignments. As in the neon matrix at 6 K, the relatively low temperature (*ca.* 100 K) of the anions in the gas phase, produced in the supersonic expansion, means that the prominent bands in the absorption spectrum originate from the lowest vibrational level in the ground electronic state. The Franck–Condon accessible vibrational levels in

the upper electronic state are then mapped out in the spectrum. The choice of the specific stretching modes excited in the upper electronic state was made on the basis of HF/6-31G** calculations carried out for the ground electronic state. Thus, the vibrational assignment has to be considered as tentative.

Table 1 Band maxima of vibrational transitions in the electronic absorption spectrum of $C_{14}H^-$ observed in a neon matrix at 6 K and in the gas phase at *ca.* 50 K

transition	ν_{gas}/cm^{-1}	ν_{matrix}/cm^{-1}
0_0^0	23 775	23 848
	23 782	
23_0^2	24 258	24 307
13_0^1	24 351	24 387
10_0^1	25 047	25 086
	25 104	
	25 338	
	25 373	
	25 445	25 483
	25 519	
$10_0^1 13_0^1$	25 606	25 676
	25 622	
8_0^1 or 16_0^2	25 761	25 833
3_0^1	26 051	26 086
	26 106	
	26 152	
10_0^2	26 210	26 267
	26 324	
	26 430	
	26 578	
$8_0^1 21_0^2$ or $16_0^2 21_0^2$	26 697	26 751
1_0^1	26 902	26 984
	26 954	
	27 021	
	27 065	
10_0^3		27 482

Tentative vibrational assignments are given, based on HF/6-31G** ground-state calculations. The error in the gas-phase values is $< 5\ cm^{-1}$, and $\pm 15\ cm^{-1}$ in the matrix.

Relation to astrophysical observations

In order to compare electronic transitions of carbon-chain type molecules observed in the gas phase with the DIBs,[7] it is necessary that the band maximum can be defined within certain error limits. A complication which exists in comparing the laboratory and astronomical data is the effect of temperature on the band profiles. The band maximum estimated from the unresolved rotational contour will shift with temperature. This can be seen, for example, in measurements on the origin band of the $A\ ^2\Pi_u$–$X\ ^2\Pi_g$ transition of diacetylene cation in a supersonic free jet.[33] A shift of 5 cm^{-1} would be apparent on passing from 300 to 10 K.

In the compilation of Table 2, only the species for which the band maximum can be

determined within ± 10 cm^{-1} are listed, but a larger uncertainty is given to accommodate for possible band maxima shifts. The data include the $^2\Pi$–X $^2\Pi$ electronic transitions of the polyacetylene cations, $HC_{2n}H^+$ ($n = 2, 3, 4$), and the related cyano-derivatives, HC_4CN^+, $NCC_{2n}CN^+$ ($n = 2, 3$), which were detected as emission spectra.[4] The most recent additions are the $^2\Pi$–X $^2\Pi$ band systems of the carbon anions, C_n^- ($n = 4$–8),[6,31,32] as well as the presently reported system of $C_{14}H^-$, all detected by resonant electron photodetachment spectroscopy. The $^2\Pi$–X $^2\Pi$ band systems of three neutral carbon chains, $C_{2n}H$ ($n = 3, 4, 5$), are the measurements *via* CRD absorption spectroscopy.

In all cases, coincidences were sought with DIBs that are claimed to have been identified (designated with + in ref. 7). For most of the molecules listed in Table 2 no coincidences were found, except for C_6^- and C_7^-. The 0_0^0 bands in the electronic spectra of these anions, at 606.8(4) nm (C_6^-) and 627.1(2) nm (C_7^-), show coincidences with DIBs situated at 606.538(4) and 627.01(3) nm, respectively. In order to check whether this is accidental, the other intense bands in the laboratory absorption spectrum were then compared.

In the case of C_7^-, the match between the laboratory frequencies of the origin and vibrationally excited bands with DIB positions is striking. This is illustrated in Fig. 5, where the laboratory spectrum (top trace) can be compared with a simulation of the tabulated values of the DIBs (bottom trace).[7] It has been proposed that, in the case of several coincidences for one specific species, two criteria should be considered.[34] First, the DIBs picked out should have comparable half-widths (FWHM) and, secondly, the ratio of the relative intensities of the laboratory bands should show a similar trend to that of the equivalent widths of the corresponding DIBs. As can be seen in Table 3, this is approximately the case for four bands of C_7^-. The FWHMs of the DIBs are comparable, and their equivalent widths are not too dissimilar to the relative laboratory intensities. The only other intense band, $1_0^1 3_0^1$, observed in the laboratory spectrum lies in a region of an intense, broad DIB at 544.96 nm. Owing to its FWHM and intensity, this belongs to another carrier and may obscure a weaker, narrow band.

Table 2 Wavelength of the origin band's maximum in the electronic transitions of carbon chains in the gas phase known with accuracy $\leqslant 10$ cm^{-1}

molecule	λ_{max}/nm	transition	ref.
C_4^-	457.1(1)	$^2\Pi_u \leftarrow$ X $^2\Pi_g$	6
HC_4H^+	506.9(3)	$^2\Pi_u \leftarrow$ X $^2\Pi_g$	4
NC_4N^+	595.8(4)	$^2\Pi_g \leftarrow$ X $^2\Pi_u$	4
HC_4CN^+	581.6(2)	$^2\Pi \leftarrow$ X $^2\Pi$	4
C_6^-	606.8(4)	$^2\Pi_g \leftarrow$ X $^2\Pi_u$	32
C_6H	526.6(1)	$^2\Pi \leftarrow$ X $^2\Pi$	
HC_6H^+	599.7(4)	$^2\Pi \leftarrow$ X $^2\Pi$	4
NC_6N^+	655.1(4)	$^2\Pi \leftarrow$ X $^2\Pi$	4
C_7^-	627.1(2)	$^2\Pi_u \leftarrow$ X $^2\Pi_g$	31
C_8^-	771.2(6)	$^2\Pi_u \leftarrow$ X $^2\Pi_g$	32
C_8H	625.9(1)	$^2\Pi \leftarrow$ X $^2\Pi$	19
$C_{10}H$	714.1(3)	$^2\Pi \leftarrow$ X $^2\Pi$	19
$C_{14}H^-$	427.7(1)	$^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$	

[a] The uncertainty given in parentheses is estimated from the data shown in the cited publications.
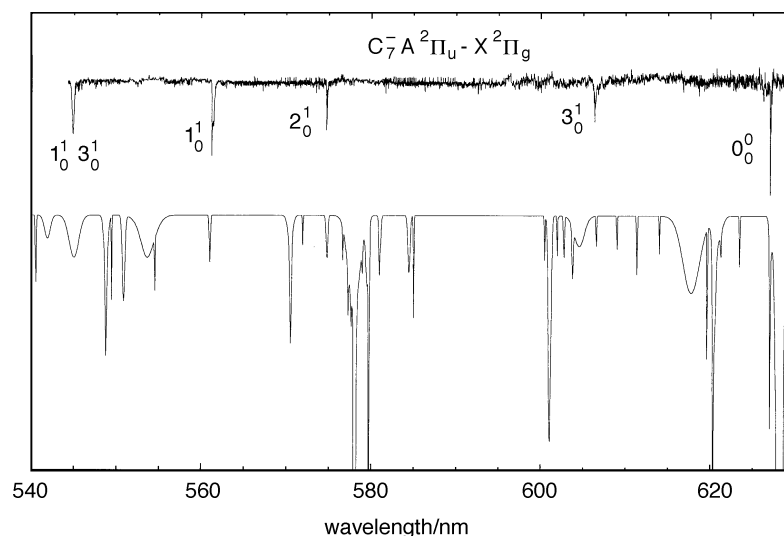
Fig. 5 Gas-phase spectrum of the $A\,^2\Pi_u \leftarrow X\,^2\Pi_g$ electronic transition of C_7^- measured in the laboratory (top trace), reproduced from ref. 31 with kind permission, and the DIBs in this wavelength region, simulated from the compilation in ref. 7

A higher-lying electronic transition of C_7^- ($B\,^2\Pi$–$X\,^2\Pi$) has been observed in the laboratory,[31] but the bands are too broad for a meaningful comparison with DIBs. This is also the case for the bands in the electronic spectra of the related anions, C_5^-, C_9^- and C_{11}^-.[31,32] Thus, on the experimental side, a goal should be to record the transitions of the latter anions under conditions similar to those achieved for the C_7^- spectrum, leading to sufficiently narrow bands for a direct comparison with astronomical data.

It has been suggested that the carriers of DIBs must have a certain size to be photostable in the interstellar radiation field. Estimates of the likely size of the molecule necessary for stability were proposed earlier as *ca.* 10–15 atoms and more recently as at least 50 atoms.[35] In view of the remarks made in the introduction of this article concerning the conclusions drawn from the observations made on the electronic spectra of carbon chains characterized in neon matrices, another goal should be the measurement of the spectra of species such as C_{2n+1} ($n > 7$), or of their isoelectronic analogues, in the gas phase.

Table 3 Comparison of the laboratory wavelengths (λ_{max}) and relative intensities (I) of vibrational bands in the $A\,^2\Pi_u \leftarrow X\,^2\Pi_g$ electronic transition of C_7^- with astronomical data[7]

	laboratory		astronomy		
transition	λ_{max}/nm	I	DIB/nm	FWHM/nm	EW
0_0^0	627.1(2)	1.0	627.01(3)	0.10(2)	0.08(2)
3_0^1	606.4(2)	0.3	606.538(4)	0.09(1)	0.014(3)
2_0^1	574.7(2)	0.5	574.781(8)	0.23(3)	0.044(1)
1_0^1	561.2(2)	0.6	560.996(23)	0.17(4)	0.035(8)
$1_0^1 3_0^1$	544.8(2)	0.5			

Band positions, FWHM and equivalent widths (EW) of the matching DIBs are tabulated.

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