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FEATURE ARTICLE

Electronic Spectroscopy of Carbon Chains

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The characteristic electronic transitions involving $\pi-\pi$ excitation have been identified for a number of homologous series of carbon chains. These include neutral species, H- and N-substituted derivatives, and ions. The absorption spectra were observed in an inert neon environment at 5 K using the approach that combines mass selection with matrix isolation spectroscopy. The understanding of the spectral pattern in the electronic transitions of carbon chains suggests the types and sizes that should be considered in connection with astronomical observations. The location of the band systems in neon matrixes has also opened the way to gas-phase studies. The first measurements on the electronic transitions of neutral carbon chain radicals by cavity ringdown spectroscopy as well as on carbon chain anions by a resonant two-photon detachment method have been made. The relevance of the spectra to the diffuse interstellar bands is illustrated.

1. Introduction

This article outlines the current state of our knowledge on the electronic spectra of carbon chains and the implications this may have on astrophysical observations. This evaluation has become possible following the detection and identification of the electronic spectra of carbon chainlike species including H or N and some of their ions. All of the initial measurements were on mass-selected species condensed in neon matrixes, but as a result of these studies, gas-phase spectra of a few such molecules have now been observed.

There are several important reasons for carrying out these investigations. (1) They lead to an understanding of the electronic spectra of carbon chains. (2) They enable one to identify the species formed by condensation of carbon vapor in matrixes and to follow their formation mechanisms. (3) They facilitate the planning and execution of gas-phase experiments because the wavelength region of the transitions has been localized. (4) These results point to certain conclusions about the relevance of such species in astrophysical observations, in particular by indicating which sort and sizes of carbon chains should be considered for gas-phase investigations, and thereby enable a direct comparison with diffuse interstellar band measurements.

Whereas the electronic spectra of C_2 and C_3 have been known since the beginning of this century and were among the earliest detected molecules in comets, only in the past two decades were those of C_2^- and then C_2^+ identified.[1] The observation and assignment of numerous spectra for homologous series of several types of carbon chains and their ions have proved possible in the past few years as a result of the development of the technique that enables mass-selected species to be trapped in neon matrixes at 5 K.[2]

The interest in the electronic spectra of the carbon chains is on several levels. Fundamentally, it leads to an understanding of the electronic structure of such species. Practically, it is a means to identify a particular molecule in terrestrial, e.g., plasmas and flames, or in astrophysical environments, e.g., comets and diffuse interstellar clouds. In an applied direction, this opens the possibility of monitoring reactive intermediates, and hence concomitant modification of conditions, in the synthesis of fullerenes for example. With these motivations in mind, the technique used to study the spectra of mass-selected cations in neon matrixes was extended to anions and neutral entities.

The only experimental information on the electronic spectra of carbon species larger than C_2 and C_3 was provided from studies of carbon vapor condensed in argon or neon matrixes.[3] This unspecific preparation resulted in the concomitant measurement of numerous species leading to profuse overlap of the spectral bands. Chemical changes could be induced by raising the temperature of the matrix, resulting in the production of other species. The approach adopted to identify several of the carrier molecules was to correlate the intensities of the UV absorption bands with identified vibrational bands in the infrared.[4,5] In connection with the latter, infrared fundamentals of a number of carbon species, C_n ($n = 4-7$, 9, 11, 13), have been observed in the gas phase by laser spectroscopy.[6] The rotationally resolved structure shows them to be linear. In fact, the C_3 and C_5 molecules have been identified in the infrared spectrum of the circumstellar shell in carbon-rich stars.[7] In the case of carbon chains with one or two hydrogens, C_nH and the cumulenes C_nH_2, microwave spectroscopy has been a notable success, identifying a number of these species in the laboratory[8,9] as well as in dense interstellar clouds.[10]

The understanding of the electronic spectra of carbon chains leads to a more profound consideration of the possible relevance to astrophysical observations. In particular, one can select the types of species and sizes that should be looked at in more detail with the specific aim of carrying out gas-phase measurements for direct comparison with astronomical measurements of the

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diffuse interstellar bands.[11] This is possible by specifying criteria that need to be fulfilled—spectroscopic so that strong absorptions are in the right region, astrophysical constraints on abundance and stability, and that the species are expected to be chemically stable and structurally sensible.

2. Electronic Transitions

The carbon chains and their hydrogen-substituted derivatives, as well as electronically related species involving nitrogen or oxygen atoms in the skeleton, exhibit similar spectral features. The strong transitions of concern are those involving the excitation of π electrons; in the language of chemistry these are either $\pi^*-\pi$ or $\pi-\pi$ type excitations. The situations encountered in the carbon chains and their ions are illustrated in Figure 1. The three cases represent either closed-shell species, such as the polyacetylenes, H(CC)$_n$H (Figure 1a) with a $^1\Sigma$ ground state, the open-shell species, e.g. C$_n$H with $^2\Pi$ ground states (Figure 1b), or the even-numbered linear carbon chains C$_n$, with $^3\Sigma$ ground state (Figure 1c). In the figure the π molecular orbitals are labeled without the g or u parity for chains with a center of symmetry. Whereas in case a the excitation is of the traditional $\pi^*-\pi$ type for closed-shell unsaturated molecules, with the excitation being dominantly represented by electron promotion from HOMO to LUMO, in cases b and c, the lowest energy strong excitation is from the penultimate occupied MO to the partially filled HOMO.

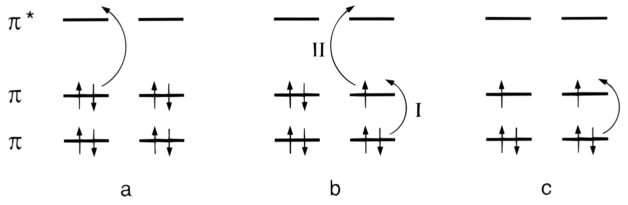

Figure 1. Types of $\pi-\pi$ excitations encountered in the electronic spectra of carbon chains.

These $\pi-\pi$ excitations possess characteristic features for a homologous series. This is well-known from the early days of MO theory of conjugated molecules, and it is exemplified most easily by the application of a simple free electron model.[12] Two main trends emerge: (1) the wavelength of the strong $\pi-\pi$ transitions (of types depicted in Figure 1) and (2) the oscillator strength of the transition; both have an approximately linear dependence on the number of heavy atoms in the chain. Thus, these $\pi-\pi$ transitions shift by similar increments, within a homologous series, toward the infrared region of the spectrum as the chain gets longer. This behavior is also one of the reasons why such systems are appealing in connection with astrophysical considerations and observations.[13] In the detection of the longer chain species, the experimental difficulties in producing them in sufficient quantities are partly compensated by the increase in oscillator strength.

3. Absorption Spectra in Neon Matrixes

The approach adopted to locate the $\pi-\pi$ transitions of chains built around a carbon backbone was to measure the absorption spectra of mass-selected species in neon matrixes.[2] The technique is conceptually simple but technically demanding. It benefits from two established methods: mass spectrometry and matrix isolation spectroscopy. The former leads to selection of cations or anions by their mass, which are co-deposited with an excess of neon to trap the species in an inert environment at 5 K. Higher concentrations of transient molecules can be attained in the matrix than in gas-phase experiments; mass-selected concentrations of $10^{15}-10^{16}$ cm^{-3} are typically accumulated in the neon matrix. The sensitivity of the measurement is enhanced by the employment of a waveguide configuration for the absorption.[14] Thus, matrixes of thickness around 150 μm are grown in about 2 h, and absorption path lengths of 2 cm are attained by propagating the interrogating light through the thin side of the matrix, parallel to the metal surface of the substrate.

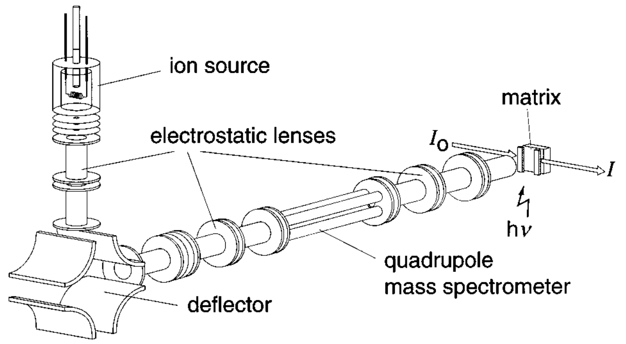

Figure 2. Schematic outline of the apparatus combining mass selection and matrix isolation spectroscopy.

A schematic layout of the instrument is shown in Figure 2. The ion source is the heart of the apparatus and is separated from the cold surface by several stages of differential pumping. Three ion sources have been developed to yield mass-selected beams with nanoampere currents: for cations and anions based on cold discharge arrangements, as well as a cesium sputter source for the bare carbon anions.[15] The former sources use acetylene or diacetylene as precursor gas, but as soon as hydrogen is present in the ionization region, the pure carbon chains are attenuated in favor of those with one or more hydrogens. Usually mass-selected currents in the nanoampere range are required for the successful detection of the absorption spectra with the waveguide approach following depositions over 1−2 h. In most experiments a mass resolution of ±3 u was usually used (adequate with cesium source), but when it was crucial to establish the number of hydrogen atoms present (with cold discharge sources), it was improved to unity. Infrared spectra of mass-selected species have also been obtained, though with sensitivities 1 or 2 orders of magnitude less than for the electronic spectra. The reason for this is twofold: first, the inherent decrease in the strength of the transition on passing to the lower frequencies in the infrared, and second, the effective path length for absorption is a fraction of a millimeter because a reflection rather than the waveguide technique is used. Thus, to compensate this somewhat, thicker matrixes are occasionally grown over ≈5 h.

3a. Polyacetylene Cations. Polyacetylene cations, HC$_n$H$^+$, and the cyano-substituted chains, HC$_n$CN$^+$ and NCC$_n$CN$^+$, can readily be formed in a cold discharge source fed on acetylene, cyanoacetylene, or cyanogen gas. The electronic spectra of the mass-selected species can then be observed following co-deposition with neon. The transitions observed are of the type $\ldots\pi^3\pi^4$ A $^2\Pi-\ldots\pi^4\pi^3$ X $^2\Pi$ (case b in Figure 1).

Figure 3 shows these electronic band systems of the HC$_n$H$^+$ homologous series, with n = even, up to HC$_{16}$H$^+$.[16] In the spectra the band to the right (i.e., low energy) is in each case the origin of the transition; the cations are at a temperature of 5 K, and thus all the transitions originate from the lowest vibrational level of the ground electronic state. The vibrational structure apparent to the blue of the origin band maps out the Franck−Condon envelope for transitions to vibrational levels

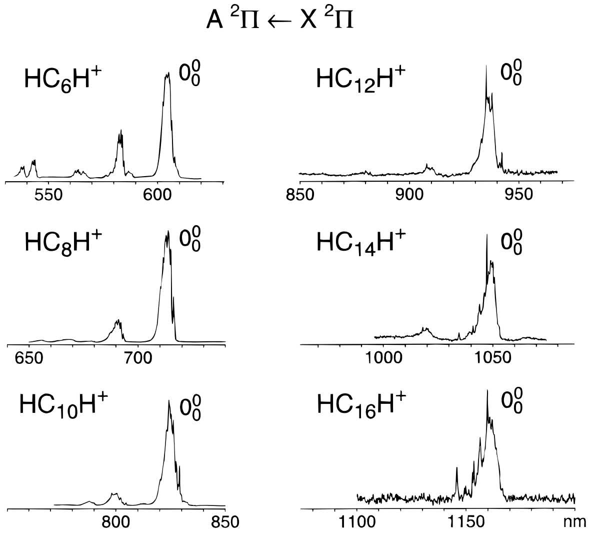

Figure 3. The $A\,^2\Pi - X\,^2\Pi$ electronic absorption spectra of the polyacetylene cations observed after mass-selected ions were co-deposited with neon to form a matrix at 5 K.

of the excited electronic state. The intense bands are due to the excitation of the totally symmetric modes, though weaker degenerate modes in double quanta are also seen. The vibrational structure is indicative of a linear−linear transition. The widths and splittings of the bands are a consequence of solid-state effects (phonon coupling and site structure) and are not of relevance here.

The characteristic feature of these spectra is the displacement of the transition energy to the red by a similar increment, ≈100 nm, with increasing chain length. When the wavelength of the origin band of these $A\,^2\Pi - X\,^2\Pi$ transitions is plotted versus the number of carbon atoms, a quasi-linear relationship is observed (Figure 4), in accordance with the simple electron in a box model.[12] This pattern is a distinct feature recurring in the homologous series involving the carbon chains and is used as a criterion for the assignment. This is in addition to (a) mass selection and (b) photobleaching experiments, which demonstrate that the species constrained in the matrix are ionic. These criteria also pertain to the identification of the spectra of the other carbon chains outlined in subsequent sections.

Complementary spectra have been detected for the HC_nH^+ species,[16] n = odd and ≤15, and that the transitions follow the same trend is seen in Figure 4, where these data (origin bands) are included. In the case of the cyano polyacetylene cations,[17] a corresponding spectroscopic pattern is discernible. As a matter of fact, when one compares isoelectronic species, e.g. HC_6H^+, HC_5N^+, and NC_4N^+, the $A\,^2\Pi - X\,^2\Pi$ electronic transitions are energetically close, with origin bands at 605, 584, and 598 nm, respectively, and manifest a similar vibrational pattern.

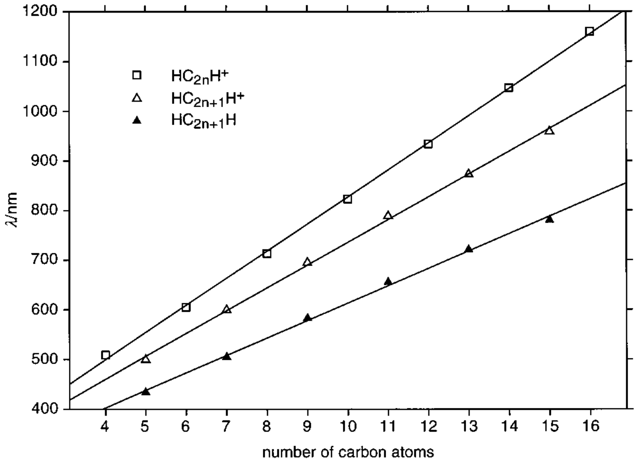

Figure 4. Approximate linear dependence of the wavelength of the origin band of the characteristic $\pi-\pi$ electronic transition of polyacetylene chains on the number of carbon atoms.

The $A\,^2\Pi - X\,^2\Pi$ electronic transitions of a number of these polyacetylene cations have been measured in the gas phase, prior to the observations in the neon matrix. This transition in HC_4H^+ was identified in 1956 as the first electronic spectrum of a polyatomic cation comprising more than three atoms.[18] The assignment was based primarily on the rotational analysis. In the 1970s the corresponding transitions of HC_nH^+, $n = 6, 8$,[19] HC_5N^+, and NC_nN^+, $n = 4, 6$,[20] were identified from emission spectra of molecular beams excited by electron impact.

3b. Neutral Polyacetylene Chains. The neutral polyacetylene chains, HC_nH and C_nH, can be characterized following primary mass selection of their cation or anions and subsequent neutralization. Both pathways have been utilized to obtain their electronic absorption spectra. In the case of HC_nH, n = odd, species, cations were co-deposited with excess neon and the neutral entities produced by recombination reactions with electrons that had been released by photon irradiation of the matrix. The $\pi-\pi$ transitions observed are of type c in Figure 1, because the ground-state configuration is $...\pi^4\pi^2$, resulting in paramagnetic species. The transitions have $^3\Sigma - X\,^3\Sigma$ symmetry, and spectra of the species up to $HC_{15}H$ have been identified.[21] As Figure 4 demonstrates, this homologous series manifests the same incremental shifts to the red with chain size as do the cations. In contrast, the HC_nH, n = even, chains are closed-shell species, showing $^1\Sigma - X\,^1\Sigma$ transitions (type a in Figure 1) in the UV. These have also been measured in the gas phase up to HC_8H.[22]

The electronic spectra of the C_nH species, n = odd, have been obtained using an anion source and electron detachment after the mass selection.[23] These radicals are open-shell species, isoelectronic with the HC_nH^+ cations, with a corresponding $^2\Pi - X\,^2\Pi$ transition (case b in Figure 1) in similar wavelength regions. Some examples are reproduced in Figure 5, and a comparison with Figure 3 illustrates these aspects. No such spectrum is observed for the C_4H molecule, because it has a $X\,^2\Sigma$ ground state, in contrast to the longer members of this homologous group.[24]

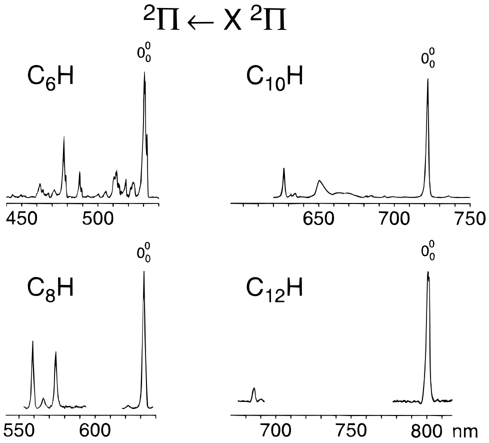

Figure 5. The $^2\Pi - X\,^2\Pi$ electronic absorption spectra of the carbon chain radicals C_nH in neon matrixes observed after mass-selected co-deposition.

The C_nH species ($n \leq 11$) have been well characterized in the gas phase by microwave spectroscopy, and precise rotational and other spectroscopic constants for the X $^2\Pi$ ground state have been obtained.[10] Some of these molecules have in fact been detected by radioastronomy in dense clouds of interstellar space, and their possible role in diffuse clouds has been pointed out.[25] Thus, the observed electronic spectra in neon matrixes are the first step toward the evaluation of their role in such environments. A few infrared bands of the carbon chain radicals, C_nH ($n \leq 6$), have been detected in argon matrixes.[26]

3c. Carbon Chain Anions. To produce copious amounts of the bare carbon anions, C_n^-, hydrogen has to be absent from the source. Thus, a cesium sputter source using a graphite substrate was developed,[15] which produced sufficient amounts of mass-selected species, so far up to C_{15}^-, to yield detectable spectra. The carbon chain anions, C_n^-, are open-shell species, with X $^2\Pi$ ground states, and are therefore isoelectronic with the polyacetylene cations, HC_nH^+, and the C_nH radicals. Because their electron affinities are considerable (e.g. 3.88 eV for C_4^-, ≈4.5 eV for C_{12}^-),[27,28] they possess more than one bound excited electronic state. These states arise from the various allowed $\pi - \pi$ and $\pi^* - \pi$ transitions (cf. excitations I and II in scheme b of Figure 1). These have indeed been observed;[29−31] as an example, the measured electronic spectrum of mass-selected C_7^- is shown in Figure 6.

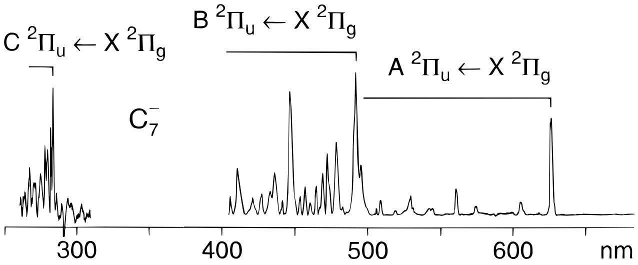

Figure 6. Absorption spectrum of mass-selected C_7^- in a neon matrix showing three electronic transitions.

The ground-state electronic configuration of C_7^- is ...$\pi_u^4\pi_g^3$ X $^2\Pi$. Three band systems are discernible,[31] with two lying at energies below the gas-phase electron affinity (≈3.4 eV).[28] The third band system, around 4.4 eV above the ground state, is observed because of the stabilizing effect of the neon environment on the excited C $^2\Pi$ state.

The simplicity of the vibrational structure for the lowest energy transition, A $^2\Pi$−X $^2\Pi$, is consistent with the assumption that it corresponds to a linear−linear (or quasi-linear) band system. The strong excitation of but a few totally symmetric modes is observed. The spectra are more complex for the higher energy transitions, indicating that vibronic effects are involved. Corresponding spectra of mass-selected C_n^- ($n = 5$, 9,11) in neon matrixes have also been observed.[31]

This technique has been extended to the measurement of the strong infrared transitions.[32] Figure 7 shows an example of such an observation; in the top trace the current of C_8^- was maximized, resulting in the concomitant observation of the C_8 infrared bands (at 1700 and 2100 cm^{-1}). Such extreme conditions had to be chosen than for recording the electronic spectra, because of the 10^2−10^3 reduction in the sensitivity in the infrared measurements (cf. section 2). In the bottom trace of Figure 7 is seen the spectrum after the anions are destroyed in the matrix by UV irradiation, leaving only the C_8 neutral peaks. By this means, a number of IR frequencies of carbon chain anions, C_n^-, $n = 5$−10, 12, have been identified.[32]

3d. Neutral Carbon Chains. The electronic configuration of neutral carbon chains with even number of carbon atoms is ....π^2, resulting in X^3 Σ_g^- ground state. The paramagnetic nature of the smaller species, C_4 to C_{10}, had already been established by ESR measurements in neon matrixes.[33] Thus, the electronic transitions expected are of type c in Figure 1 and correspond to $^3\Sigma_u^-$−X $^3\Sigma_g^-$ symmetry. In the gas phase, rotationally resolved IR spectra have proved the linearity of C_4 and C_6 in their ground states.[34]

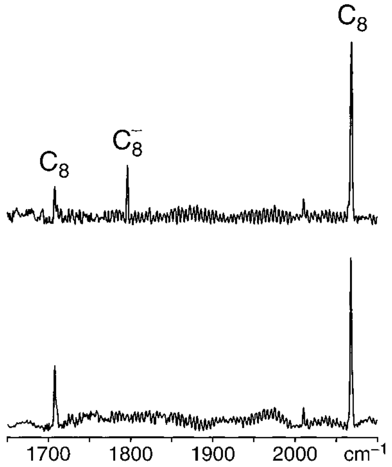

Figure 7. Infrared bands of C_8^- and C_8 discernible in a neon matrix after mass selection (top trace). The bottom spectrum shows the infrared bands of C_8 only, because the anions were destroyed by UV irradiation of the matrix.

The $^3\Sigma_u^-$−X $^3\Sigma_g^-$ electronic transitions of C_4,[35] C_6,C_8,[23] and C_{10}[30] could be detected after mass selection of their anion and photodetachment either during or after co-deposition with neon to form the 5 K matrix. The spectra are depicted in Figure 8 and show the expected monotonic shifts toward lower energies with increasing size. The vibrational structure is typical of linear−linear transitions; for example, in the case of C_4, the intense bands comprise progression and combination series involving two (ν_1 and ν_2) of the three totally symmetric stretching modes.

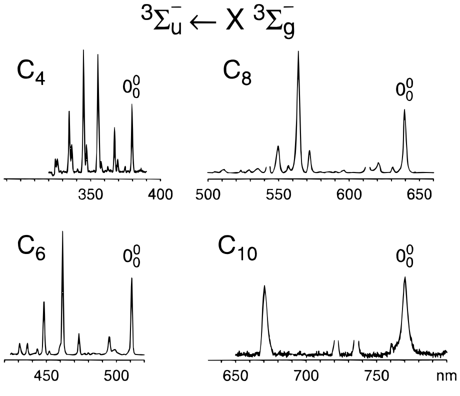

Figure 8. The $^3\Sigma_u^-$−X $^3\Sigma_g^-$ electronic transition of the even-number carbon chains in neon matrixes. Mass-selected anions were co-deposited with neon, and the photodetachment was accomplished by UV irradiation of the matrix.

Though the spectrum of C_{10} could also be detected (Figure 8), the intensity of the band system is smaller than expected by comparison with data for the smaller members of this homologous series. Furthermore, no analogous transitions could be detected for C_{12} or C_{14}, although the spectra of their anions, C_{12}^- and C_{14}^-, are easily observed.[30] On photobleaching these systems disappear and the anions are destroyed, but the expected transitions of their neutral counterparts do not appear at energies extrapolated on the basis of the observations made for C_4−C_{10}. Some new bands are seen at other energies, and these may be

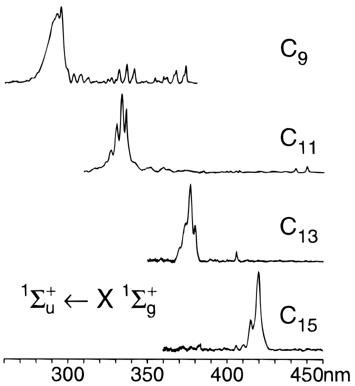

Figure 9. The $^1\Sigma_u^+$−X $^1\Sigma_g^+$ electronic transitions of the odd-number carbon chains in neon matrixes. These were prepared by mass selection of their corresponding anions and subsequent photodetachment in the matrix.

candidates for nonlinear C_{12} and C_{14} molecules. These observations thus provide direct experimental evidence that the geometrical structure of the carbon species with even number of carbon atoms changes after C_{10}. Both theoretical calculations[36] and photoelectron spectra of carbon anions[27,37] indicate linear geometries for C_{2n} ($n \leq 5$) but monocyclic ones for the larger neutral species.

In contrast, the electronic transitions of linear carbon chains with an odd number of carbon atoms are readily detected (Figure 9).[38] The upper mass, C_{15}, has so far been limited by the experimental capabilities and not by structures that cease to be chains beyond this size. These molecules have closed-shell ground-state configurations ...π^4 X $^1\Sigma_g^+$, and the characteristic transitions (scheme a in Figure 1) are of $^1\Sigma_u^+$−X $^1\Sigma_g^+$ symmetry. The regular shifts to lower energy (≈40−45 nm) with number of carbon atoms can be used to predict the wavelength region of this transition of C_3, hitherto unidentified, near 170 nm. In the gas phase the IR spectra of the species C_{2n+1} ($n = 1-6$) have been obtained, and the rotational structure is that expected for linear chains.[6]

4. Gas-Phase Measurements

The aim of the studies to locate the electronic transitions of mass-selected species in neon matrixes is to be able ultimately to characterize these species in the gas phase. With the knowledge of the wavelength region of the sought-after band system, the planning and execution of measurements in the gas phase becomes a realistic proposition. The expected gas-neon matrix shifts can be estimated based on both sets of data available for a number of species. These shifts can be in the 100−200 cm^{-1} range for $\pi-\pi$ transitions for the longer chain species. Nevertheless, this uncertainty is small enough to make a search in the gas phase attractive. With this strategy, the detection of the B $^4\Sigma_u^-$−X $^4\Sigma_g^-$ transition of gaseous C_2^+ was readily accomplished[39] following its detection in a neon matrix.[40]

It should be noted that the electronic transitions of a number of polyacetylene cations have been detected as emission spectra in the gas phase quite sometime ago (see section 3a).[19,20] In the following two sections, the recent studies of the electronic spectra of gas-phase carbon anion and neutral chains by two different approaches, resulting from the observations in neon matrixes, are outlined.

4a. Carbon Anion Chains. The electronic transitions of a number of carbon anion chains have now been studied in the gas phase. All the experiments are based on resonant photodetachment spectroscopy. The first study by one-color resonance-enhanced photodetachment was on the $^2\Pi$−X $^2\Pi$ transition of C_5^-, showing a broad origin and vibrationally excited band.[41] Following the identification of the A $^2\Pi$−X $^2\Pi$ transition of the carbon chain anions with even number of carbon atoms in a neon matrix[23] (section 3c), these band systems for C_4^-, C_6^-, and C_8^- were detected in the gas phase by a two-color photodetachment process.[42] In case of C_4^- the origin band of this transition could be rotationally resolved and analyzed.[43] The most recent have been the one-color studies of the A $^2\Pi$−X $^2\Pi$ band system of C_7^-, C_9^-, and C_{11}^-.[44] Though vibrational structure is discernible, the bands are relatively broad.

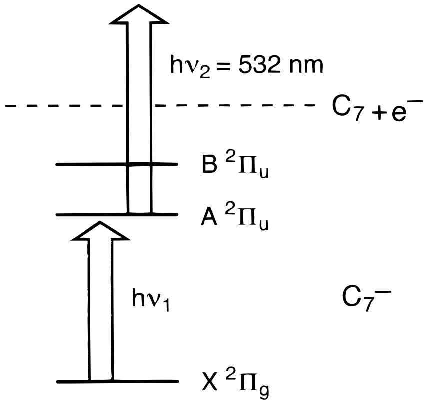

Figure 10. The two-color resonant phototodetachment approach used to observe the electronic transitions of C_7^- in the gas phase.

Narrower bands are obtained using a two-color photodetachment scheme and a pulsed supersonic discharge source to produce the carbon anions.[45] This is illustrated for C_7^-, where the B $^2\Pi$−X $^2\Pi$ and A $^2\Pi$−X $^2\Pi$ transitions have been located in the neon matrix (Figure 6).[31] In the gas phase the two-color scheme depicted in Figure 10 can be used to probe these transitions. The first photon ($h\nu_1$) from a tunable dye laser induces a bound−bound transition, e.g. A $^2\Pi$−X $^2\Pi$, whereas the second photon ($h\nu_2$, 532 nm Nd:YAG laser) causes the photodetachment. The resulting spectrum is shown in Figure 11.

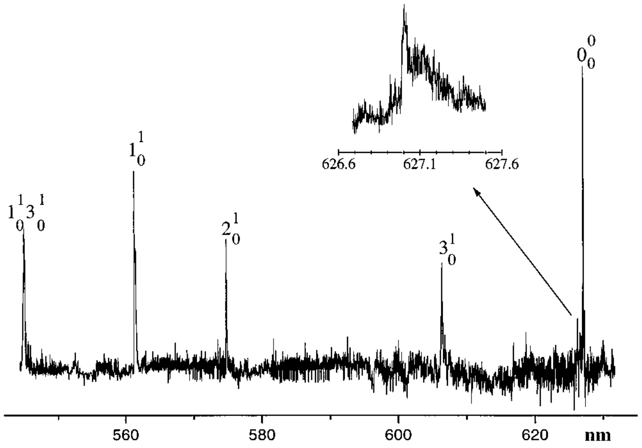

Figure 11. The A $^2\Pi$−X $^2\Pi$ electronic transition of C_7^- measured in the gas phase by the two-color laser excitation scheme depicted in Figure 10. The inset is a higher resolution scan of the origin band.

Compared to an earlier report,[44] the bands are about 2 orders of magnitude narrower, the difference being attributed to the lower temperature of the anions as well as to reduction of power broadening. The spectra show the excitation of three totally symmetric stretching modes. The origin band is shifted by 11 cm^{-1} to the lower energies relative to the value in a neon matrix.

In an analogous manner the B $^2\Pi$−X $^2\Pi$ transition can be mapped out. Corresponding observations have been made on the B $^2\Pi$, A $^2\Pi$−X $^2\Pi$ transitions of C_5^- and the C $^2\Pi$−X $^2\Pi$ one of C_9^-.[45]

4b. The C_6H Radical Carbon Chain. An attractive approach for the detection of the electronic transitions of carbon chains appears to be cavity-ringdown spectroscopy.[46] This technique, essentially direct absorption with path lengths in the 10−20 km range, has been successfully used to detect minute concentrations of molecules and transient species in environments ranging from static cells to flames.[47] It has also proved possible to detect the A $^2\Pi_u$−X $^2\Sigma_g^+$ transition of N_2^+, with an oscillator strength of 10^{-5}, in a hollow cathode discharge.[48] This method was then used to record the A $^2\Pi$−X $^2\Pi$ electronic spectrum of the carbon chain radical, C_6H. The transition had been previously located in a neon matrix.[23]

A mixture of acetylene in excess of helium was used to produce C_6H. The discharge was operated in a pulsed mode, 60 μs width, 1.5 A current. The 1 m long hollow cathode is located between the two highly reflective mirrows. A pulsed laser fired 20 μs after the end of the discharge induced the absorption, and the decay curve is accumulated. The decay characteristics indicate that path lengths of over 20 km are attained.

The absorption spectrum of the $^2\Pi$−X $^2\Pi$ transition of C_6H observed[49] is seen in Figure 12. In contrast to the spectrum in the matrix (Figure 5), in the gas phase pairs of bands are apparent, associated with the two spin−orbit components: $^2\Pi_{1/2}$−X $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$−X $^2\Pi_{3/2}$. At the 5 K temperature of the neon matrix, only the lower lying X $^2\Pi_{3/2}$ $v = 0$ level is populated. The origin ($\Omega = {}^3/_2$) band is shifted by ≈131 cm^{-1} to the blue of the matrix value.

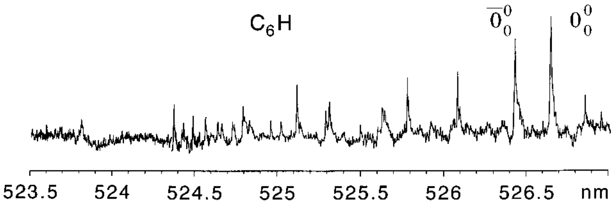

Figure 12. The $^2\Pi$−X $^2\Pi$ electronic transition of C_6H measured in the gas phase by cavity ringdown spectroscopy in a hollow cathode discharge.

The detection limit of cavity ringdown spectroscopy has been estimated at $I/I_0 \leq 10^{-7}$. Assuming the expected $(2-3) \times 10^{-2}$ oscillator strength for this $^2\Pi$−X $^2\Pi$ transition leads to an estimated C_6H concentration of around 2×10^8 cm^{-3} in the discharge. This is comparable with the density of this radical in the discharge cell used for its detection by microwave spectroscopy.[50]

5. Gas-Matrix Shifts

As considerable amount of spectroscopic data on carbon chains, both neutral and ionic, have now been obtained in neon matrixes, the knowledge of the magnitude of gas-matrix shifts is desirable, in particular for comparison with astronomical measurements. These results are summarized in Figure 13.

Generally the shifts are to lower energies on passing from the gas phase to neon, and the shift increases with size of the species. The exception are the smaller carbon anions where the shift is to the blue (e.g. C_4^-), but it goes over to a red shift for the longer ones (e.g. C_6^-), similarly to the other chains. Cations and neutrals with same number of carbon atoms manifest comparable dispacements: e.g., HC_6H^+, ≈135 cm^{-1}; C_6H, ≈131 cm^{-1}. The isoelectronic cyanopolyacetylene cations have smaller shifts (Figure 13). The significant trend is that the shift appears to level out for the longer species. In view of these data, gas-phase energies can probably be predicted to within 50 cm^{-1} on the basis of the values observed in a neon matrix. This is sufficient for searches in the laboratory to be undertaken, but on the other hand, the uncertainty is still too large for direct comparisons to be made with astronomical data.

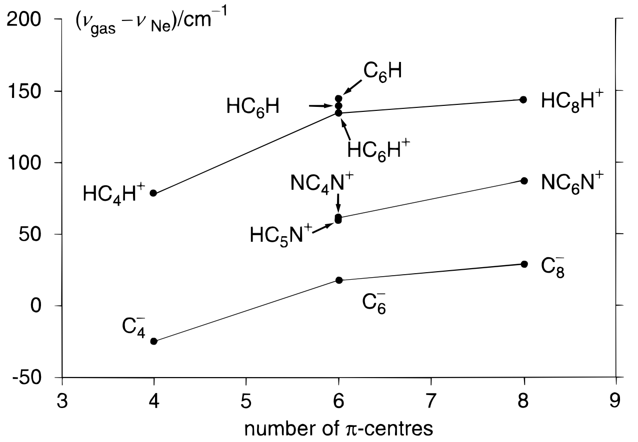

Figure 13. Variation of the gas-neon matrix shift of the $\pi-\pi$ electronic transitions of carbon chains. The positive values imply that the gas-phase frequencies are at higher energies.

6. Relation to Astronomical Observations

The question addressed is which type and sizes of carbon chains (including those with H, N, and O) should be considered as relevant in connection with astrophysical phenomena; in particular, which of these molecules should be considered as possible carriers of the diffuse interstellar bands (DIBs).

That carbon chains are attractive candidates as some of the absorbers resulting in the DIBs was initially proposed by Douglas,[51] though he focused on the smaller bare carbon chains. The detection by radioastronomy of a number of carbon chain radicals, C_nH ($n = 4$−8), the cumulenes C_nH_2 ($n = 2$, 3), and the cyanopolyacetylene chains, up to $HC_{11}N$ in dark clouds,[10] has also activated the interest in their consideration in diffuse regions.[52]

A more detailed appraisal of this proposition can now be made by applying spectroscopic, chemical, and astrophysical constraints to the size and type of carbon chains. These in turn enable one to decide which species should be of primary interest for attempts to measure electronic transitions in the gas phase. Clearly, one has to be more selective here, as systematic measurement in the gas phase, in much the same way as in the neon matrix, is too onerous a task.

The astronomical measurements indicate that 100−200 DIBs are located in the 400−900 nm region.[11,53] Thus, from the regular shifts of the intense $\pi-\pi$ transitions to the red with length of a carbon chain, the appropriate size of the molecules required for these band systems to absorb in this wavelength range can be determined. For chains based on the carbon skeleton, but not yet spectroscopically characterized in a neon matrix, this can also be predicted by comparison with isoelectronic or electronically related species. This aspect is illustrated in Figure 14 where the $^2\Pi$−X $^2\Pi$ absorption spectra of isoelectronic species are displayed. All these chains absorb at energies within $^1/_2$ eV of each other.

The carbon chains that could easily be present in diffuse clouds are C_n, C_nH, HC_nH, and the C_nH_2 isomers and their ions

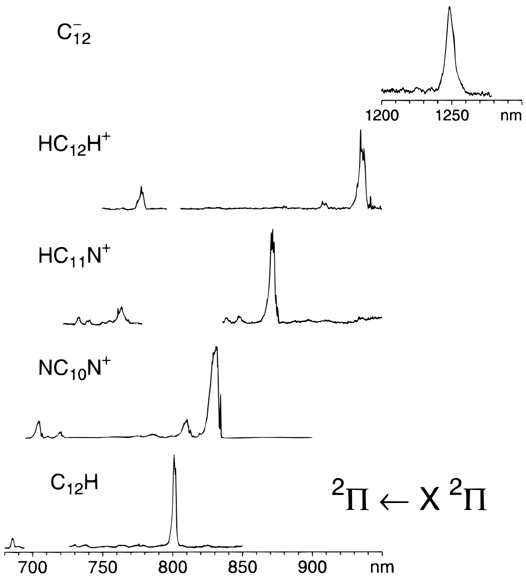

Figure 14. The $^2\Pi - X\ ^2\Pi$ electronic absorption spectra of isoelectronic carbon chain species. These were measured in neon matrixes using the mass-selected technique.

as well as related N- and O-containing molecules. The first question to answer is, which types of these species would have their strong $\pi - \pi$ transitions in the 400−900 nm region? Among the bare neutral carbon chains, C_n, the ones with $n =$ even terminate at C_{10} (cf. section 3d), so only the $n =$ odd, 17 to upper 30's, remain. Among the anions, C_5^- to C_8^- absorb in this wavelength range, and for these molecules gas-phase measurements have already been carried out (section 4a). If the uncertainty in the determined vibrational band maxima are taken to be in the 5−10 cm^{-1} range, then a match is found for the origin band of the A $^2\Pi - X\ ^2\Pi$ transition of C_6^- and C_7^- with DIB positions.[54] In the case of C_7^- several of the more intense bands involving vibrational excitation in the upper state seen in the laboratory spectrum show striking matches. This can be seen in Figure 15 where the laboratory spectrum (top trace) and the astronomical DIB measurements are compared. The origin and the next three prominent vibrationally excited transitions show remarkable agreement with the DIBs. Not only are the band maxima within 0.2 nm of each other, but also the widths of the DIBs are comparable and their equivalent widths follow the trend of the intensities of the laboratory spectrum.[54] These criteria have been proposed for a successful confirmation.[55] A similar comparison was made with the available gas-phase data on the polyacetylene and cyanopolyacetylene cations (section 3a) as well as for C_6H, all of which have strong electronic transitions in the DIB region, but without success.[54]

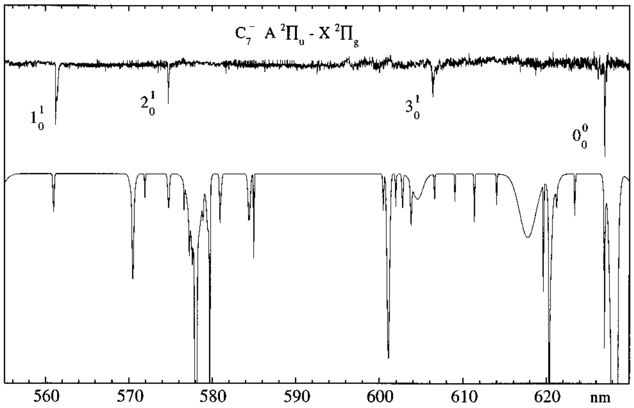

Figure 15. Comparison of the laboratory gas-phase spectrum of the A $^2\Pi_u - X\ ^2\Pi_g$ electronic transition of C_7^- (top trace) with the astronomical observations of diffuse interstellar bands (bottom spectrum, constructed from the data compilation of ref 53).

It has often been argued that the molecules have to be large enough to be stable with respect to photodissociation in the stellar radiation field. Estimates of the necessary size range from 10 to 15, to at least 50 atoms.[56] If the former criterion is applied, then one is left with the carbon chains $C_{17}-C_{37}$ and the isoelectronic $C_{2n+1}H^+$, $C_{2n}N^+$ ($n > 9$), and related species. However, chemical considerations and calculations seem to indicate that at certain size the chain networks are replaced by other structures, e.g. cyclic- or fullerene-like.[57] Ion mobility experiments indicate this structural change in carbon anions and cations.[58] Thus, there may well be a natural limitation for the length of carbon chains.

The electronically related species with similar spectroscopic properties will include the cumulenes, C_nH_2. This has been investigated so far only theoretically and leads to the prediction that cumulenes with sizes $C_{13}H_2$ to around $C_{34}H_2$ have their first strong electronic transitions in the 400−900 nm range.[59] Similarly, the C_nO species with $n =$ odd and X $^1\Sigma_g^+$ ground states[60] will behave spectroscopically in a similar way to the C_{2n+1} species.

7. Outlook

The identification and understanding of the characteristic electronic spectra of a number of homologous series of carbon chains in neon matrixes has opened the way to studies in the gas phase and to a consideration of their possible relevance to the diffuse interstellar band phenomenon. Once the energy of a transition has been localized, gas-phase searches using a variety of laser-based techniques become feasible. The results of the first such measurements have now emerged, both for carbon anions and for the neutral C_6H chain. For the astrophysical connection, the criteria specified for the species to possess the necessary spectral signatures as well as being physicochemically reasonable, suggest targeting measurements on larger carbon chains. Provided that these can be produced in sufficient concentrations, a number of sensitive spectroscopic approaches, such as those illustrated in this review, could be applied in the gas-phase characterization.

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