

ON THE POSSIBLE ROLE OF CARBON CHAINS AS CARRIERS OF DIFFUSE INTERSTELLAR BANDS

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ABSTRACT

Because the laboratory gas-phase electronic spectra of only the three polyatomic bare carbon chains C_3 , C_4 and C_5 are available, we have made a further attempt to detect the origin bands of C_4 (3789 Å) and C_5 (5109 Å) in the diffuse cloud toward ζ Oph. The measurements provide an improved 3 σ limit to their column densities: $N(C_4) \leq 5 \times 10^{11} \text{ cm}^{-2}$ and $N(C_5) \leq 1 \times 10^{11} \text{ cm}^{-2}$, with a signal-to-noise ratio (S/N) of 42,000 and 31,000 Å⁻¹, respectively, at a resolution of 110,000. The limits to $N(C_4)$ and $N(C_5)$ are lower than predictions from the chemical model used by Roueff and coworkers for such diffuse clouds. In conjunction with observations of related, hydrogen-containing polar chains in the millimeter region and laboratory studies of the electronic transitions of a number of homologous series, these results lead to interesting conclusions about the role of carbon chains as potential carriers of the diffuse interstellar bands (DIBs). First, the abundance and oscillator strength of smaller chains, say up to 10 atoms, are too small to account for the stronger DIBs. Second, because of the electronic configurations of these open-shell species, the lowest energy π - π transition does not have a large oscillator strength but the higher energy one in the UV does, and the chains would have to be prohibitively long for these absorptions to shift into the DIB 4000–9000 Å wavelength region. The exceptions are closed-shell systems such as the odd-numbered bare carbon chains, and the ones in the C_{15} – C_{31} size range that have their very strong transitions in this region. These species should be a major goal for laboratory and subsequent astronomical studies.

Subject headings: astrochemistry — ISM: lines and bands — ISM: molecules

1. INTRODUCTION

Ever since the suggestion that carbon chains should be considered as possible carriers of the diffuse interstellar bands (DIBs) (Douglas 1977; Smith, Snow, & York, 1977), it has been clear that this hypothesis could only be tested when laboratory gas-phase electronic spectra of some prototype systems were available. There are two associated aspects: understanding which sort of carbon chains would have strong electronic transitions in the region where most of the DIBs are observed (4000–9000 Å), and the successful development of techniques in the laboratory to obtain the spectra under the conditions of interstellar space. Taking the bare neutral carbon chains, C_n , as an example, although the electronic spectra of C_2 and C_3 have been known for a long time, no other gas-phase electronic spectra were available until a few years ago. Knowledge of the electronic spectra of longer carbon chains came from observing them in neon matrices at 6 K using mass-selected beams (Maier 1998). As a result, the electronic transitions of the species C_5 , C_7 , ..., C_{21} were experimentally observed (Forney et al. 1996; Wyss et al. 1999), as well as C_4 , C_6 , ..., C_{14} (Freivogel et al. 1996).

With these data in hand, one could select the chains with transitions in the DIB range and design experiments to detect

them in the gas phase. In the case of the neutral chains, this has so far only proved possible for C_4 (Linnartz et al. 2000) and C_5 (Motylewski et al. 1999). These electronic transitions were observed by producing the carbon chains in a discharge plasma in a supersonic free jet and detecting their absorption by the cavity ringdown method. From these studies one can predict the rotational profile of these electronic transitions at a chosen temperature.

Because C_4 and C_5 , in addition to C_3 , remain the only polyatomic carbon chains with available gas-phase electronic spectra, it was clear that these spectroscopic signatures provided an important opportunity to look for them in the more diffuse medium. The identification of C_3 through its origin band at 4052 Å (Maier et al. 2001) led to several further studies in diffuse and translucent clouds (Roueff et al. 2002), including correlations with C_2 (Oka et al. 2003; Ádámkóvics, Blake, & McCall 2003). Subsequently, we reported the results of our first attempt to detect C_4 and C_5 in diffuse clouds (Maier, Walker, & Bohlender 2002). Although the transitions sought were not visible, we derived upper limits to the column densities. In the astronomical measurements we achieved a signal-to-noise ratio (S/N) of $\sim 2000 \text{ pixel}^{-1}$ at a resolution of 110,000. In a subsequent article reporting predictions of a chemical model for these molecules (Roueff et al. 2002), it was remarked that we must have been rather close to their detection.

Encouraged by this prediction and a new theoretical study of the oscillator strength of the studied transition of C_4

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(Jungen & Xu 2003), a further attempt at detection was undertaken in 2003. Estimation of column densities relies on reliable oscillator strengths of the electronic transitions used for the measurement, which, in the case of C₄ and C₅, are only available from theory and are the main source of uncertainty. The new theoretical result for C₄ yields an f -value of 0.003 for the ${}^3\Sigma_u^- - X{}^3\Sigma_g^-$ transition (with the origin band at 3789 Å and $f_{0-0} \approx 0.0006$), which is more than a factor of 10 larger than given by Mühlhäuser et al. (2000), but the same as an earlier report (Pacchioni & Koutecky 1988). Thus, the chances of detecting C₄ and C₅ (for which the f_{0-0} value of the 5109 Å band was estimated as 0.001; Maier et al. 2002) were considered equivalent because the abundance of C₄ is predicted to be nearly double that of C₅ (Roueff et al. 2002). As these are the only polyatomic carbon chains (except for C₃) for which a direct comparison can be made between laboratory and astronomical data, these provide valuable bench marks for models of diffuse cloud chemistry and lead to important implications as the type and size of carbon chains which should now be focused on as potential DIB carriers.

In this paper we summarize the current situation in the context of laboratory studies carried out in recent years on not only bare carbon chains, but also their ions and simple derivatives containing hydrogen or nitrogen. The subtle difference in the electronic structure of the species shows that not only is the right spectral signature required, but also a transition with large oscillator strength. This, in fact, leads to considerable selectivity and restricts the molecules that can be considered relevant for future studies. The results presented here on C₄ and C₅ provide the basis for many of the conclusions.

2. OBSERVATIONS

Usable spectra were taken of ζ Oph (HD 149757) and η UMa (HD 120315), a rapidly rotating standard, on five half nights, 2003 June 11–15 (UT). The spectrograph was the Gecko echellette, fiber fed from the Cassegrain focus of the Canada-France-Hawaii 3.6 m telescope (CFHT) (Baudrand & Vitry 2000). The setup and observations exactly parallel those reported for the 2001 run, and details can be found in Maier et al. (2002).

As with the 2001 run, use of an incandescent lamp for flat-fielding at 3789 Å proved inadequate, so spectra of η UMa were used instead. Low-order polynomial fits to Th/Ar arc lines were used to calibrate the ζ Oph spectra for wavelength, and the spectra were aligned to the velocity of the K I 4044.1 and 4047.2 Å interstellar lines as listed in Maier et al. (2001), thereby putting any interstellar features on a laboratory scale.

The data from the 2003 run were combined with those from the 2001 run (Maier et al. 2002). The combined, unsmoothed spectra are compared in Figure 1 to the laboratory data. Nothing in the astronomical spectra matches either of the bands. These gas-phase spectra were measured a few years ago (C₅, Motylewski et al. 1999; C₄, Linnartz et al. 2000), and their analysis led to the determination of the rotational constants in the excited electronic states, which are given in the two articles. The profiles shown in Figure 1 are almost like the ones actually observed, which were recorded at a resolution comparable to that of the astronomical spectra, with the exception that lines of C₂, which are present in the laboratory spectra, have been removed. The gas-phase spectra show only

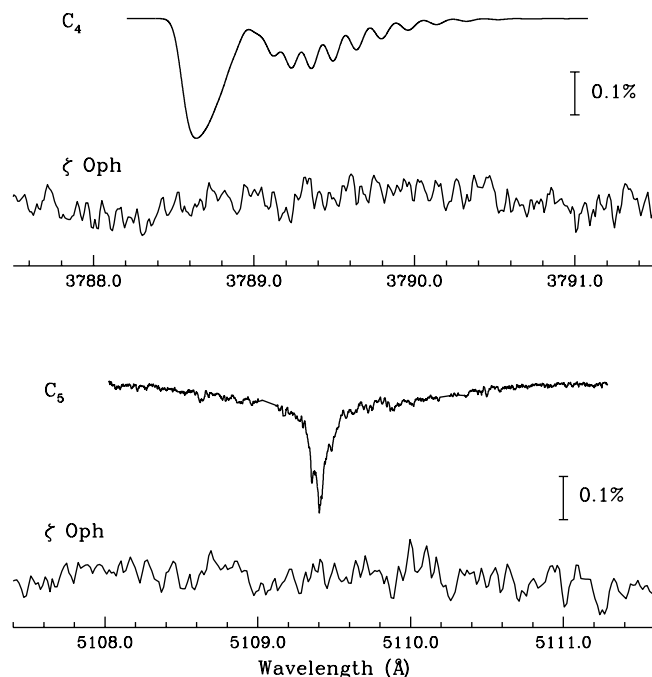


FIG. 1.—Comparison of C₄ and C₅ laboratory spectra with those observed for ζ Oph at CFHT. The spectra of ζ Oph are unsmoothed and are the sum of those taken in 2001 and 2003. The gas spectra of C₄ and C₅ shown are the profiles predicted from the rotational constants inferred from infrared (ground state) and electronic spectra (excited state) in the gas phase, at a temperature of 80 K and a resolving power of 110,000, but broadened to the linewidth actually observed in laboratory measurements (as discussed in Maier et al. 2002).

partial resolution of the rotational structure as a result of broadening due to intramolecular processes. Thus, whereas the P lines in the spectrum of C₄ are still distinct but broadened, in the R head (the broad peak to the blue) the overlap smears out the details. Nevertheless, the rotational constants in the excited electronic state have been deduced from the ground-state constants, which were determined from high-resolution infrared spectroscopy and then by fitting the observed rotational profiles. The rotational profile can then be predicted for a chosen temperature.

For comparison with the astronomical measurements, the predicted spectra at 80 K are shown in Figure 1 for C₄ and C₅. The line width due to the intramolecular process is actually larger than the instrumental broadening at the resolution of 125,000 we used at the telescope. A temperature of 80 K is chosen because nonpolar molecules will not cool down efficiently; the measurements of the electronic spectrum of C₃ (Maier et al. 2001) show this directly, where the temperature inferred from the intensity distribution of the rotational structure is 80 K. The change in the predicted profiles for C₄ and C₅ on going to 20 K is slight and does not alter in any significant way the estimations of the upper limits of the column densities discussed in § 3.

After removing a low-order polynomial from the spectra in Figure 1, histograms of residuals from each mean were generated; these are shown in Figure 2. The best-fitting Gaussians correspond to $\sigma = 2.27 \times 10^{-4}$ or S/N = 4400 per 0.0109 Å pixel at 3789 Å, and $\sigma = 2.56 \times 10^{-4}$ or S/N = 3900 per 0.0155 Å pixel at 5109 Å. The Gaussian fit seems quite satisfactory at 3789 Å, implying that precision was principally limited by photon shot noise, but the fit is less convincing at

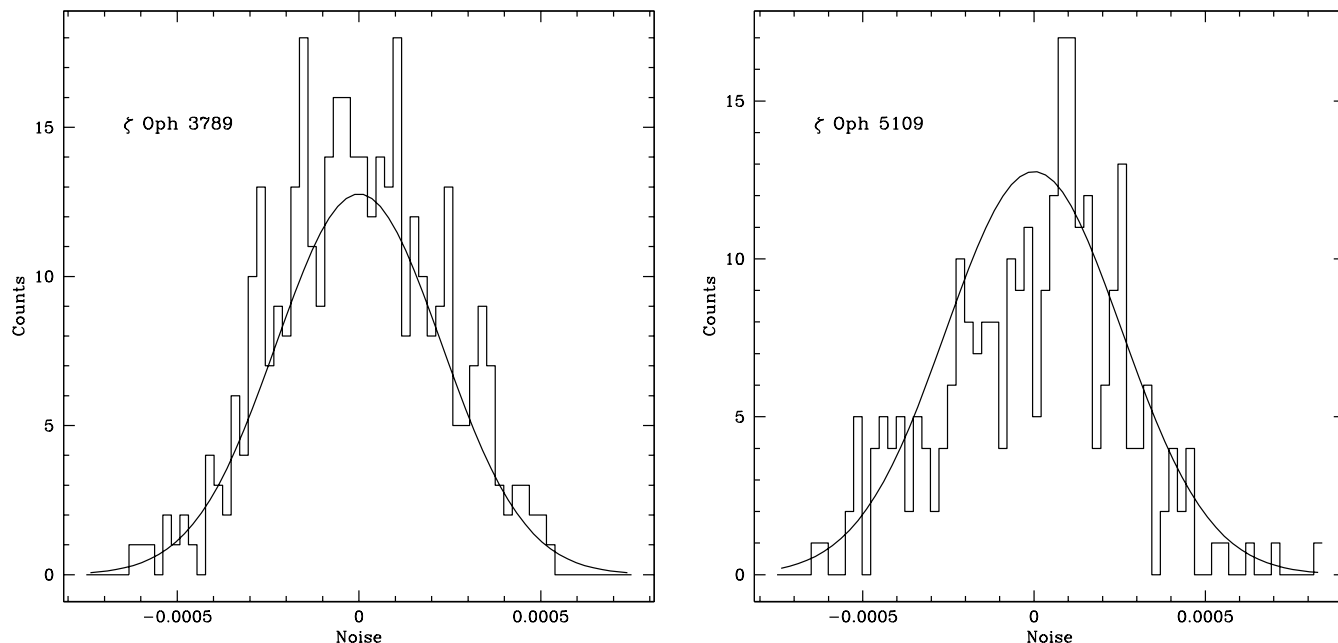


FIG. 2.—Error histograms for the unsmoothed spectra of ζ Oph at 3789 Å (*left*) and 5109 Å (*right*) shown in Fig. 1, after removal of low order polynomials. The best-fitting Gaussians correspond to $\sigma = 2.27 \times 10^{-4}$ and 2.56×10^{-4} , equivalent to $S/N = 4400$ per 0.0109 Å pixel and 3900 per 0.0155 Å pixel at 3789 Å and 5109 Å, respectively.

5109 Å, where there might be an additional noise contribution. For comparison with other studies, the S/N we achieved are equivalent to 42,000 and 31,000 Å $^{-1}$ at 3789 and 5109 Å, respectively.

3. COLUMN DENSITIES

We derived 3 σ detection limits from

$$W_{\max} = 3(wd)^{1/2}(S/N)^{-1},$$

where the 3 σ limiting equivalent width, W_{\max} , and the FWHM of the laboratory feature, w , are both measured in Å; the spectrograph dispersion, d , in Å pixel $^{-1}$; and S/N is the signal-to-noise ratio per pixel. We adopted $w = 0.24$ and 0.13 Å, for the laboratory features, and $d = 0.0109$ and 0.0155 Å pixel $^{-1}$ at 3789 and 5109 Å, respectively.

The above calculation gives $W_{\max} = 3.5 \times 10^{-5}$ Å for both the C_4 and C_5 laboratory features in Figure 1. The limits to the column densities, $N(C_4)$ and $N(C_5)$ can now be derived from W_{\max} using the usual equation

$$N_{\max} \text{ (cm}^{-2}\text{)} = \frac{1.13 \times 10^{20} W_{\max}}{\lambda^2 f},$$

but with the new value, $f = 0.003$, for the C_4 transition (Jungen & Xu 2003), leading to $f_{0-0} \approx 0.0006$, when the Franck-Condon factors of the vibrational bands are considered; λ is the wavelength in Å. In the case of C_5 , the previously used f_{0-0} value of 0.001 has not changed. This results in the column densities $N(C_4) \leq 5 \times 10^{11}$ cm $^{-2}$ and $N(C_5) \leq 1 \times 10^{11}$ cm $^{-2}$. These values can be compared directly to the prediction of the UMIST chemical network, modified by Roueff et al. (2002, Fig. 5), in which the values $N(C_4) \approx 1 \times 10^{12}$ cm $^{-2}$ and $N(C_5) \approx 7 \times 10^{11}$ cm $^{-2}$ appear for a diffuse cloud with $A_v \approx 1$, which applies toward ζ Oph. The prediction of N from the model for C_3 is close to the observed value of 2×10^{12} cm $^{-2}$, but the column density for C_5 is about 7

times higher than our limit and in the case of C_4 , higher by a factor of 2.

We have considered the possibility of improving on this in the future. In the case of C_4 , at least a factor of 2 was lost in signal by using the fiber rather than the coudé UV mirror train, and there should also be a factor of 5 gain with an 8 m class telescope. In addition, the oscillator strength of the $1_0^1 2_0^1$ C_4 band at 3440 Å is a factor of 2 larger than for the 3789 Å origin band. Ádámkóvics et al. (2003) have found diffuse clouds with a factor of 10 higher column density of C_3 (e.g., HD 204827) than toward ζ Oph. A S/N of $\sim 15,000$ Å $^{-1}$ could be achieved for HD 204827 at 5109 Å with a few nights' observation on an 8 m class telescope, but it is probably too faint at 3789 Å.

4. DISCUSSION: DIBs AND CARBON CHAINS

The detection of C_3 and the upper limits to the abundances given here for C_4 and C_5 in diffuse clouds, together with the understanding gained in the numerous recent laboratory gas phase studies in Basel on homologous series of radicals and ions with a carbon chain skeleton (see e.g., Ding et al. 2003), enable us to draw rather interesting conclusions about what species are relevant as possible carriers of DIBs. Also pertinent is millimeter-wave spectroscopy of a number of polar carbon chains with hydrogen substituents, in the diffuse medium (Lucas & Liszt 2000).

In the case of the three carbon species C_3 , C_4 , and C_5 , the bands in the electronic transitions used for the search have low oscillator strengths ($f_{0-0} \sim 0.016$, 0.0006, and 0.001, respectively), making it difficult to detect them; the absorptions of individual rotational lines for C_3 in ζ Oph have equivalent widths of ≈ 0.1 mÅ. These species have another electronic transition $^1\Sigma_u^+ - X^1\Sigma_g^+$ in the UV (near 1700 Å for C_3 and 2400 Å for C_5), or $^3\Sigma_u^- - X^3\Sigma_g^-$ (near 2000 Å for C_4) with unity or more oscillator strength, which has been observed in neon matrices but not in the gas phase. Using the transition for C_3 would not lead to any new insight, since

the column density has already been determined, whereas for C₄ or C₅ this could lead to detection limits of at least 2 orders of magnitude lower than at present.

Some of the C_nH molecules (e.g., $n = 3, 6, 8$) do have electronic transitions in the DIB region (Maier 1998). A comparison of the abundances determined for species observed in dense clouds with those in translucent and diffuse clouds, e.g., C₂H, C₃H₂ (see, for example, Table 2 of Lucas & Liszt 2000; Turner 2000), shows that these are a bit lower or comparable in translucent clouds and may be even a factor of 10 less in the diffuse environment. If we then consider C₆H, which has a column density in dense clouds of around 10^{12} cm⁻² (Turner 2000), then we can assume that this will be at most in the 10^{11} – 10^{12} cm⁻² range in diffuse clouds. This radical has its origin band of the $^2\Pi - X^2\Pi$ electronic transition at 5266 Å (Motylewski et al. 2000), with calculated oscillator strength $f_{0-0} = 0.02$ (Cao & Peyerimhoff 2001). With these values we can then predict that a DIB at 5266 Å would have an equivalent width of ≈ 1 mÅ, which is barely detectable. A similar comparison has been made for the linear radicals C_nH, $n = 3, 5, 7$, (Ding et al. 2002). Thus, although these sorts of polar carbon chains are readily detectable at millimeter-wavelengths, their identification via electronic transitions is currently much more difficult and clearly cannot be responsible for the stronger DIBs, which have equivalent widths of the order of 0.1 Å (Herbig 1995).

Consequently, carbon chains and their simple derivatives, containing up to, say, 10 atoms, can be excluded as carriers of the strong DIBs; this begs the question of which systems should now be considered. In view of the above we can specify these criteria:

1. They must have electronic transitions in the DIB (≈ 4000 – 9000 Å) region; and
2. Their column densities either have to be 2 orders of magnitude larger than that observed for C₃, or the oscillator strengths of the transitions have to be in the range 1–10.

Column densities above 1×10^{14} cm⁻² are unlikely to be attained for polyatomic chains. It has also been argued that the lack of detectable IR emission expected from carbon chains may constrain the general abundance of these species (Allamandola et al. 1999). However, the larger systems do possess electronic transitions with f -values of 1–10 in magnitude.

The oscillator strength of an allowed electronic transition of a carbon chain grows with size (Watson 1994). However, in most cases the lowest energy band system of a particular symmetry (Σ - Σ or Π - Π) does not have a large intensity. This aspect is best illustrated by an example from our laboratory

studies and by reference to Figure 3. If one has a closed shell system, such as the C chains with an odd number of carbon atoms, C_{2n+1}, then the energetically lowest, strongest transition $^1\Sigma_u^+ - X^1\Sigma_g^+$ (which results from $\pi^*-\pi$ excitation) has a large oscillator strength, increasing with size. For C₃ this transition is around 1700 Å with $f \approx 1$, whereas for C₁₅ this is around 4000 Å with $f \approx 5$ expected by scaling with the chain length. If, however, one has open-shell systems (i.e., the highest occupied molecular orbital is partially filled), then the lowest transition of Σ - Σ or Π - Π symmetry has a lower oscillator strength, whereas the one of the next higher energy has f -values of unity or more. This is a well-known phenomenon of open-shell species, arising from configuration interaction (the transitions are a mixture of the $\pi^*-\pi$ and $\pi-\pi$ excitations, see Fig. 3), and was rationalized theoretically a long time ago (Dewar & Longuet-Higgins 1954). The even-carbon chains, C_{2n}, are an example of this: the first $^3\Sigma_u^- - X^3\Sigma_g^-$ transition (e.g., the 3789 Å system of C₄) has a small oscillator strength ($f = 0.003$ for C₄), but the next, $2^3\Sigma_u^- - X^3\Sigma_g^-$, is intense (around 2000 Å for C₄) and has $f \approx 1$, according to theory (Mühlhäuser et al. 2000).

Thus, regarding the types of longer carbon chains for consideration as good candidates for the stronger DIBs, we see that not only do the transitions have to be in the DIB range, but they also have to possess a large oscillator strength. This leads to a considerable restriction in the choice of systems and in fact make the odd-numbered chains, C_{2n+1}, somewhat unique. The species C₁₅ to C₃₁ will have their $^1\Sigma_u^+ - X^1\Sigma_g^+$ electronic systems in the 4000–9000 Å region with f -values in the 5–10 range. Other molecules, e.g., the polyacetylenes, HC_{2n}H, which also possess this transition with similar f -values (Pino et al. 2001), would have to be very long (say 40 or more carbon atoms) to absorb in the DIB range.

Similar arguments will apply to the open-shell species that have a strong transition to higher energy: they will have to be extremely long for their electronic absorption bands to lie in the visible. For example, in the case of the even carbon chains, C_{2n}, the strong $2^3\Sigma_u^- - X^3\Sigma_g^-$ transition lies near 3300 Å for C₁₀ (Grutter et al. 1999) and only C₂₀ and larger systems would move above 4000 Å. However, such long, even-numbered chains have not been identified, and theory predicts that cyclic forms are preferred, further limiting the selection.

4.1. Conclusion

The conclusion of this analysis is that the carbon-chain systems that would seem to satisfy the criteria necessary to be DIB carriers would all have to be very long (e.g., the HC_nH,

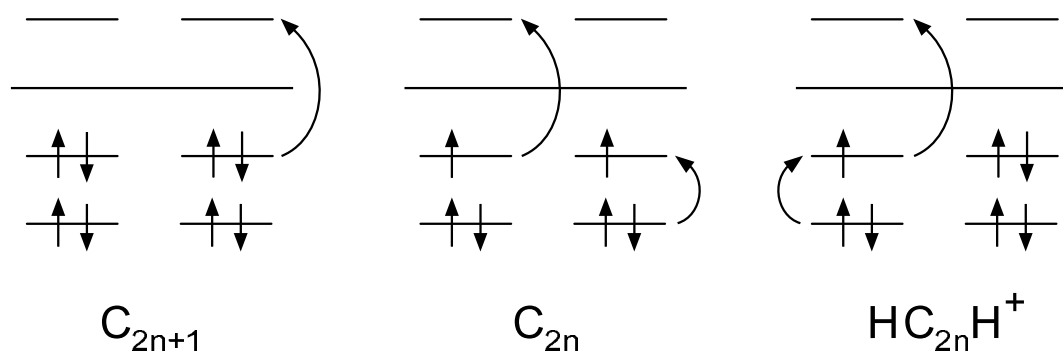


FIG. 3.—Ground state electronic configuration of the highest occupied molecular orbitals of the carbon-chain radicals and ions discussed in the text. The electron excitation involved in the relevant transitions is indicated.

C_{2n} , C_nH neutral chains; the HC_nH^+ cations; or the $(C_n)^-$ anions), except for the odd-numbered carbon chains. The latter, and the isoelectronic (e.g., $C_{2n+1}H^+$) and related chains (e.g., $C_{2n}O$), appear to be the natural choice for laboratory studies in the coming years.

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