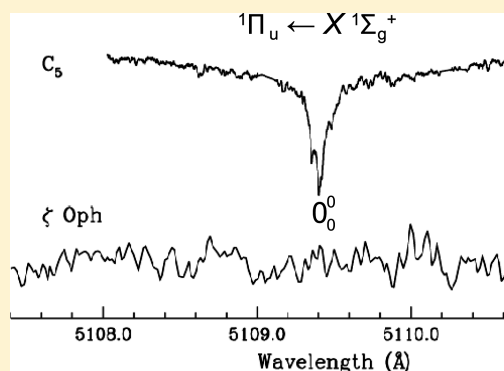


Electronic Spectroscopy of Carbon Chains and Rings of Astrophysical Interest

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ABSTRACT: This perspective is concerned with laboratory measurements of the electronic spectra of carbon chains, rings, and their ions, including derivatives terminated by hydrogen and nitrogen atoms. The selected species have relevance to astronomical observations through diffuse clouds, absorption features known as diffuse interstellar bands (DIBs). Two indications to decide which molecules should be studied are the observations of polar carbon chains in dense clouds by rotational spectroscopy and the knowledge that a certain number of these have electronic transitions in the DIB region. This information has been obtained initially by measurements of the electronic absorptions in 6 K neon matrixes using mass-selection. This was followed by the gas-phase observations using cavity ringdown and resonance enhanced techniques in combination with pulsed-supersonic discharge sources or via laser vaporization. The gas-phase spectra were then compared with DIB data, all with negative results, except for the detection of C_3 , but leading to upper limits of their column densities $<10^{12} \text{ cm}^{-2}$. By reference to mm-wave absorption measurements in the diffuse medium, it is shown that, although species such as H_2C_3 are present there, the product of the expected column densities and oscillator strength of the transitions will lead to only very weak DIBs. The significant conclusion is that carbon chains and their derivatives containing hydrogen or nitrogen comprising up to a dozen atoms cannot be responsible for stronger DIBs. However, chains with an odd-number of carbon atoms, C_{17} , C_{19} , ..., have very intense transitions in the region above 4400 Å and remain attractive candidates. An uncertainty is the excited electronic state lifetime; if this is less than 70 fs, then the resulting absorptions would be too broad to be astronomically relevant. The electronic absorptions of some of the species studied bear a striking resemblance to DIB data. The two peaked rotational contour of the origin band in the electronic transition of dicyanoacetylene cation is superimposable on a DIB absorption when shifted by 1 Å. The band profiles of cyclic C_{18} at 100 or 20 K are similar to DIBs but differ in wavelength. This suggests that another set of potential candidates are the carbon rings of sizes up to a hundred of atoms, including ions and heavy atoms, with the requirement of a large oscillator strength. Observations on the absorptions of propadienylidene C_3H_2 and C_{60}^+ are discussed.



1. INTRODUCTION

This perspective is concerned with the measurement of the electronic spectra of transient molecules containing predominately carbon. These include bare carbon chains and rings, their simple derivatives terminated with hydrogen and/or nitrogen, and their ions. The emphasis is on those that are deemed important for comparison with astronomical observations in the optical region. Astronomers have identified absorption bands in the 4000–9000 Å wavelength region, presumed to arise from gas-phase molecules present in diffuse interstellar clouds. These are known along numerous lines of sight in our galaxy as well as external ones.^{1,2} The absorption features are the diffuse interstellar bands (DIBs). Since their discovery a century ago,³ the number detected has grown up to around six hundred with improved detection methods.¹ They are characterized by different widths, intensities, and shapes showing partial rotational structure or asymmetry. Their identification remains elusive.

In the last two decades, conclusions have been derived from the comparison of laboratory gas-phase electronic spectra of carbon based radicals and ions and the DIB measurements.⁴ Though these have not led to an identification of a single carrier,

spectroscopic knowledge and insight gained provide clues for current and future studies of possible candidates. In addition, because one has observed for the first-time the electronic spectra of numerous organic radicals, this has potential use in other areas of chemistry such as the means of identifying them in situ as intermediates in flames and plasmas and to monitor chemical dynamics.⁵

The problem of choosing appropriate molecular systems has been approached with two main considerations: (1) knowledge of molecules in the interstellar medium (ISM), which have been identified unambiguously by radio astronomy, and (2) expectation that the species will have electronic transitions in the optical region. Furthermore, the molecules should be chemically reasonable.

Until about 20 years ago most of the discussions as to the nature of the DIB carriers were mainly speculative, even bacteria were suggested,⁶ or based on spectra of stable molecules mainly in solution.⁷ With the development of sensitive, sometimes

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mass-selective, methods in chemical physics including molecular beams, discharges, and lasers, one could attempt to measure the electronic spectra of specific molecules in the gas phase. Fluorescence was initially used to detect the electronic transitions of organic radical cations.⁸ This was too restrictive for the species targeted according to the two criteria given above as the majority of polyatomic systems do not fluoresce. This led to the use of cavity ringdown techniques using both pulsed⁹ and continuous-wave¹⁰ lasers, resonance enhanced two-photon schemes on neutrals,¹¹ anions,¹² and later on mass-selected cations confined in traps.¹³

Two influential developments took place 30–40 years ago: (1) the detection of numerous polar carbon chains, e.g., C_6H , cyanopolyacetylenes in dense interstellar clouds and (2) thoughts on the photochemical properties of larger systems, notably by Douglas.¹⁴ DIBs lack clear rotational structure, not necessarily due to predissociation, which could be associated with lifetime broadening but also to intramolecular processes: internal conversion or isomerization. Douglas states “long carbon chain molecules C_n where n may lie in the range $n = 5–15$ ” are viable DIB candidates.¹⁴ Thus, the measurement of the electronic spectra of such species and those already detected in the dense clouds was required. It remained to be determined which molecular systems would have strong electronic transitions in the DIB region. Certainly some of the carbon chains have this characteristic but only those of a restricted size.⁴ Hydrogen substituted carbon chains $C_{2n}H$ ($n = 2–4$) observed in dense clouds, belong to this category. However, the neutral cyanopolyacetylenes, including the largest interstellar molecule detected $HC_{11}N$,¹⁵ are closed shell species with electronic transitions in the UV. However, if they were ionized and there is discussion in the astrophysical community that both the cations and anions of larger molecules may be equally important as their neutral precursors,¹⁶ then they would have transitions in the visible. With this background information, measurements of electronic spectra in the gas-phase of such species in the laboratory and the first-time direct comparisons with DIB data could be made.

2. ELECTRONIC TRANSITIONS OF CARBON CHAINS

Consider the isoelectronic species, C_6H , C_6^- , HC_6H^+ , and NC_4N^+ . In order to search for their electronic transitions in the gas-phase, it proved advantageous to locate these first in neon matrixes at 6 K using a mass selective method.¹⁷ One could accumulate sufficient concentrations, around 10^{13} – 10^{14} cm⁻³, of mass-selected species in neon matrixes. Then the whole wavelength range from the UV to near IR can be measured with an absorption technique. This proved to be successful, and the electronic transitions were located, enabling a gas phase search with an uncertainty estimated to be merely 100 cm⁻¹.

The current apparatus is shown in Figure 1. A number of ion sources are employed, from cesium sputter for the bare carbon species to a hot-cathode one for cations. The requirement is that ~ 1 nA of mass-selected species have to be produced. After extraction and mass selection, the ions are codeposited with an excess of neon (typically $1:10^6$) on a rhodium-coated sapphire plate held at 5–6 K. Matrixes are grown to 100–200 μ m thickness in 3–5 h, and absorption is used to interrogate the molecules of interest. White light is focused into the matrix and undergoes total internal reflection over a path length of 20 mm. The exiting light is collected on an optical bundle, dispersed and detected with a CCD camera.¹⁸ Currently, the 250–950 nm region can be scanned in one hour.

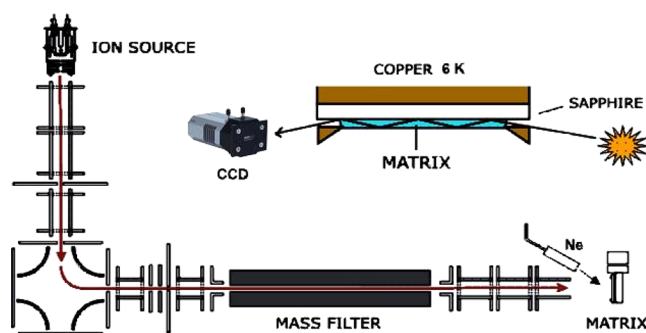


Figure 1. Experimental apparatus used for mass-selected deposition in neon matrixes.

In this manner the absorption spectra of the four isoelectronic molecules shown in Figure 2 have been obtained. An analysis of

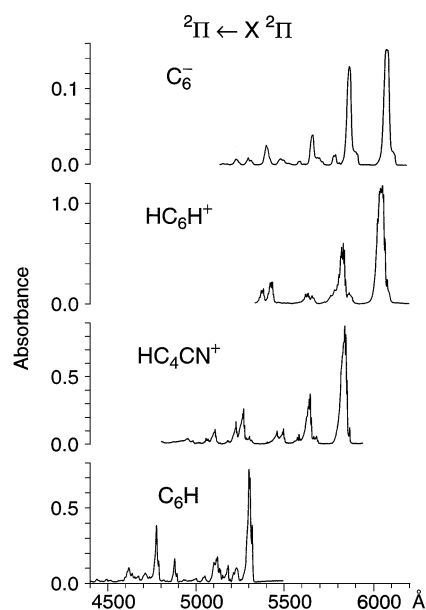


Figure 2. The $2\Pi \leftarrow X^2\Pi$ electronic transition of the isoelectronic species measured in absorption in 6 K neon matrixes.

the vibrational pattern and considerations of electronic structure (and calculations if necessary) confirm that these are linear open-shell species having a $2\Pi \leftarrow X^2\Pi$ transition.⁵ The origin band wavelength indicates where gas-phase measurements should be conducted; for $\pi \leftarrow \pi$ transitions of the organic radicals, a redshift in the range 50–150 cm⁻¹ in neon matrixes is expected. In Figure 3, the origin band position of $\pi \leftarrow \pi$ electronic transitions versus the number of carbons in the chain is shown. The strongest transition is the $1^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ for chains with an odd number of carbon atoms. Few of these lie in the 4400–9000 Å DIB region. There are only a finite number of stronger DIBs, and therefore, discrimination, chemical and/or spectroscopic, is a must, as provided by carbon chains. Another characteristic that helps both the laboratory experiments and detection of the larger species in the ISM is that the oscillator strength of the transition scales roughly linearly with the size as equations in Figure 3 show. In the ISM, this has allowed the detection of $HC_{11}N$ even though its abundance is much lower than for shorter chains. One can see that not all carbon chains C_n $n = 5–15$ will absorb in the visible and that some of the transitions are weak.⁴

Among the carbon chains, C_5 shows a weaker $1^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition around 520 nm, whereas its $1^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ system at 240 nm is

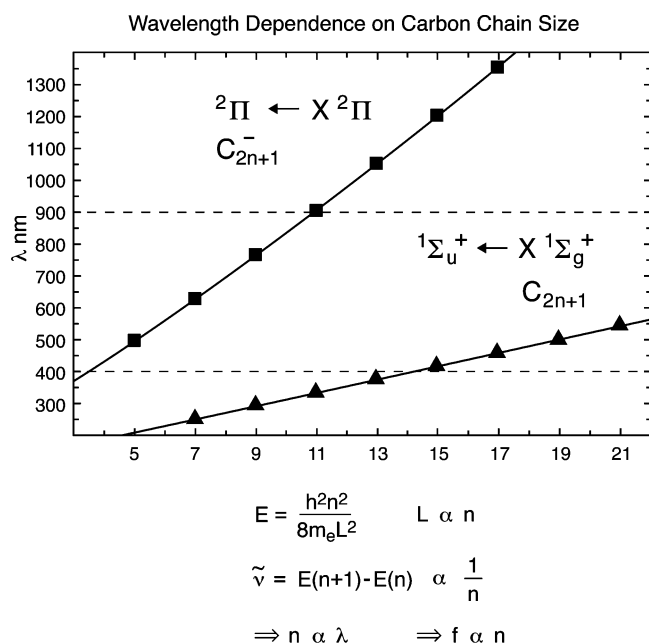


Figure 3. Wavelength of the origin bands in neon matrices in the π – π electronic transitions of C_{2n+1} ($1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$) and C_{2n+1} ($A^2\Pi \leftarrow X^2\Pi$) versus the number of carbon atoms.

2 orders of magnitude stronger. Moreover, the shorter wavelength absorption for the chains C_{17} and C_{19} will be in the DIB region and very strong ($f \approx 1$ – 10). The four isoelectronic species in Figure 2 have moderately intense ($f \approx 0.05$) transitions in the visible. Thus, a start to unravelling the DIB mystery was to obtain the gas-phase electronic spectra of these transient molecules in the laboratory.

The most recent studies using mass-selection and neon matrices have enabled us to obtain the electronic absorption spectra of protonated pyrene and coronene. They show distinct absorptions in the visible and thus are now a focus of gas-phase measurements. The $S_1 \leftarrow S_0$ electronic transitions are in the DIB region and have moderate oscillator strengths. That of protonated coronene is shown in Figure 4. The corresponding neutrals have also been observed, obtained by neutralization of the cations in the matrix. These may also be of interest to astrophysics; for example, the origin band of the $(3)^2A' \leftarrow X^2A'$ transition of the coronenyl radical is at 4699 Å in a neon matrix (Figure 4).

2.1. Gas-Phase Spectra. In the gas-phase, the transient species of interest, such as carbon chains and those shown in Figure 2, can be prepared in a supersonic expansion through which a discharge runs or by laser vaporization of graphite.¹⁹ Depending on the conditions, different size chains, rings, and fullerenes can be made as has been shown by mass spectrometry.⁴ In the discharge source, acetylene diluted in helium or mixtures containing a source of nitrogen can produce the species of Figure 2. The electronic spectra of C_6H , HC_6H^+ , and NC_4N^+ could then be detected by cavity ringdown spectroscopy (Figure 5). A supersonic slit jet expansion was used producing radical concentrations on the order of 10^{10} cm^{-3} . This is sufficient to detect the absorption in the gas phase. Figure 6 shows the case of the $A^2\Pi \leftarrow X^2\Pi$ electronic spectrum of C_6H (bottom trace). One can see the blueshift (~ 50 – 150 cm^{-1}) compared to the absorption in the neon matrix (top). In the gas-phase spectrum, the rotational structure is resolved, and by using the $X^2\Pi$ ground state constants,¹⁹ known from mm-wave spectroscopy and used

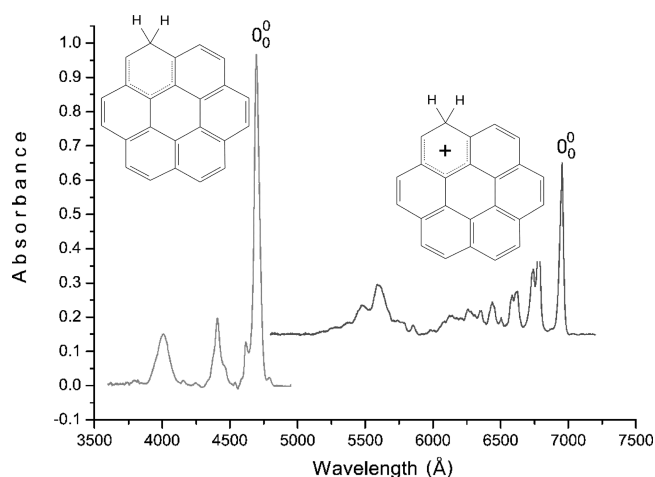


Figure 4. Electronic absorption spectrum of the $(1)^1A' \leftarrow X^1A'$ transition of protonated coronene and the $(3)^2A' \leftarrow X^2A'$ system of coronenyl radical in 6 K neon matrices.

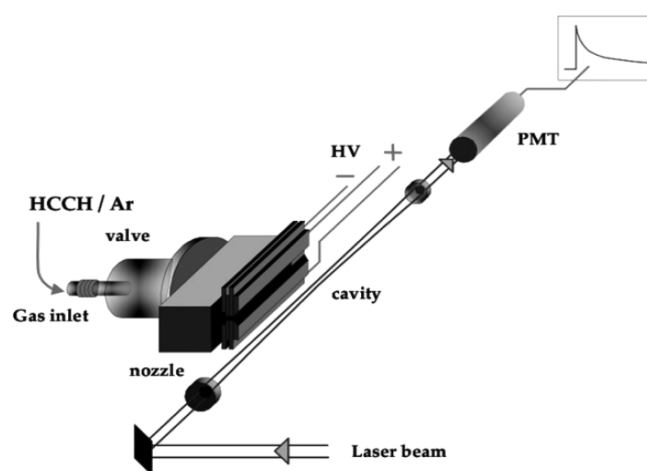


Figure 5. Cavity ringdown setup for the measurement of the absorption spectra of species created in a pulsed supersonic discharge.

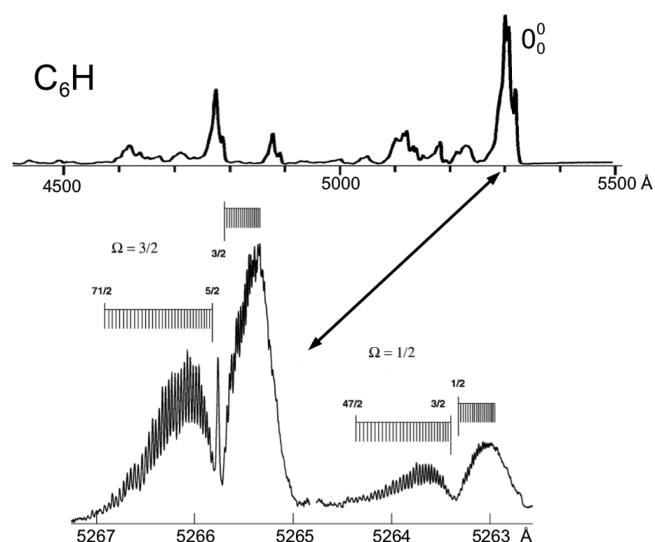


Figure 6. Electronic spectrum of the $^2\Pi \leftarrow X^2\Pi$ transition of C_6H measured in a 6 K neon matrix (top) and the origin band in the gas-phase (bottom). Adapted with permission from ref 20. Copyright 1999 Elsevier.

to identify the species in dense interstellar clouds, the analysis yields the corresponding values for the excited $^2\Pi$ state.²⁰ Subsequently, for comparison with DIB data, the band profile can be predicted at temperatures appropriate for molecules in the diffuse clouds, taking into account the velocity dispersion within the cloud. Though the telescope resolution is usually around 0.1 Å, the observed atomic lines²¹ are much broader (~ 0.5 Å).

The $^1\Pi_u \leftarrow X^1\Sigma_g^+$ origin band of C_5 using the laboratory observations at 80 K is illustrated in Figure 7 and compared to a specific

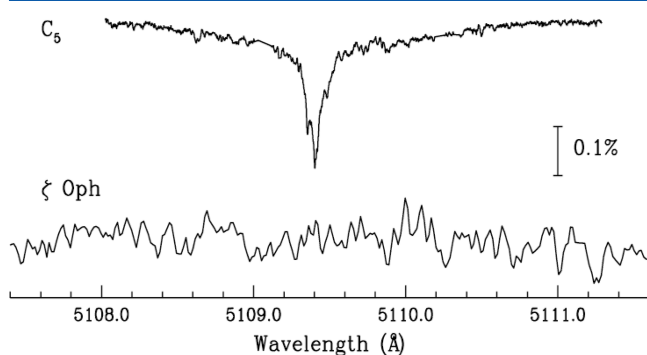


Figure 7. Origin band of the $^1\Pi_u \leftarrow X^1\Sigma_g^+$ electronic transition of C_5 measured in the laboratory at 80 K in comparison with astronomical data observed through diffuse clouds toward ζ Oph. Adapted with permission from ref 27. Copyright 2002 Institute of Physics.

astronomical search in this wavelength region toward reddened stars. The interstellar absorption was not apparent.²² However, an upper limit to the column density of C_5 in the diffuse cloud can be inferred using the wavelength of the transition, the detection limits of the astronomical data, and the oscillator strength (obtained by a theoretical calculation). A similar comparison of the laboratory spectra with absorptions in the DIB region has been carried out for quite a few species: C_5 , $HC_{2n}H^+$ $n = 2-4$, $HC_{2n}CN^+$ $n = 2,3$, $NCC_{2n}CN^+$ $n = 1,2$, and carbon chain anions C_n^- and HC_n^- , all merely leading to upper limits of the column density, i.e., less than $\sim 10^{12} \text{ cm}^{-2}$. The implications of this are discussed by two examples.

The electronic transitions of $I-C_3H$ were obtained using a discharge jet expansion and resonant two photon ionization technique. The spectrum is complex comprising several electronic systems.¹¹ The lowest energy transition, $A^2A' \leftarrow X^2\Pi_{1/2}$, has an origin band at 5210.4 Å and was compared to DIB data with a negative result.¹¹ However, $I-C_3H$ has also been observed by radio astronomy in dense clouds, and in translucent ones with a column density of around 10^{12} cm^{-2} .²³ Taking this abundance and the theoretically calculated oscillator strength ($f \approx 0.01$) of the transition leads to the prediction that a DIB at 5210 Å would have an equivalent width (EW) of 0.1 mÅ, which is below the usual detection limit. The general conclusion on these sorts of molecules is that undoubtedly these are present in the diffuse clouds; however, the combination of their column densities ($\sim 10^{12} \text{ cm}^{-2}$) and oscillator strengths ($f \approx 0.01-0.1$) cannot lead to the stronger DIBs. This refutes the statement in Douglas' paper¹⁴ that bare carbon chains such as C_5 , C_6 , ..., C_{15} are potential candidates. In fact, the significant conclusion from these gas phase spectra and comparison with DIBs is that carbon chains up to a dozen atoms, as well as their cations or anions, or their related simple derivatives containing H or N are not responsible for the stronger DIBs.

This inference can be turned round to ask the question which molecules would have the right spectroscopic properties to be

suitable DIB candidates for future laboratory studies? So far, C_3 is the only carbon chain that was detected in diffuse clouds by means of its $^1\Pi_u \leftarrow X^1\Sigma_g^+$ electronic transition at 4052 Å. The EW of the rotational lines observed was weak, of the order of mÅ, indicating a C_3 column density of $10^{11}-10^{12} \text{ cm}^{-2}$ depending on the cloud sampled.²⁴ Assuming this column density and choosing systems with oscillator strengths 3 orders of magnitude larger than that of C_3 leads to the conclusion that the linear carbon chains C_{17} , C_{19} , ..., with very strong ($f \approx 1-10$) $^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ electronic transitions in the visible, are appealing as DIB candidates. Their absorption could give rise to stronger DIBs with EW around 0.1 Å. Similar arguments can be applied to isoelectronic species containing O, N, and H. Even though the electronic spectra of the latter molecules have not yet been measured in neon matrixes, approximate locations of their transitions are readily predicted.⁵

Attempts to obtain the electronic spectra in the gas-phase of C_{15} , C_{17} , ..., using ns pump-probe excitation with an F_2 ionization laser have failed.²⁵ A reason for this may be that the $^1\Sigma_u^+$ excited states of these carbon chains have short lifetimes. Current measurements with ps lasers confirm this.²⁶ This restricts the number of species that are astrophysically relevant. In addition to the spectroscopic requirement that the transitions lie in the DIB range and that they possess oscillator strengths of the order of unity, electronic excited-state lifetimes must be greater than ~ 70 fs, otherwise the width of the bands is too large to be DIB relevant. The lifetime is determined by intramolecular processes and is specific to each molecule; a priori it is not possible to predict it. In the observation of the $^1\Pi_u \leftarrow X^1\Sigma_g^+$ electronic transition of C_5 (Figure 7), it was noted that intramolecular processes were already limiting the resolution of the rotational structure.²⁷ Studies of the relaxation routes led to a 5 ps lifetime for the excited electronic state levels;²⁵ thus, even in a molecule as small as C_5 band broadening can be significant.

3. SIMILARITIES OF LABORATORY ABSORPTIONS AND DIBS

The attempt to measure the $^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ electronic transitions of C_{15} and C_{17} so far have not been successful even though the species are readily produced by laser vaporization as mass spectrometry shows. However, one could observe the absorptions of C_{14} , C_{18} , and C_{22} rings, members of the Hückel $4n + 2$ aromatic family.²⁸ Several excited electronic states are apparent. In the case of C_{18} , only the absorption at 5928 Å is of interest for an astronomical comparison because the bands of the higher states are too broad (>100 Å). The origin band of the $A^1A'_2 \leftarrow X^1A'_1$ transition is shown in Figure 8. The rotational profile varies with temperature from 100 to 20 K, which is achieved experimentally by changing the expansion conditions. The rotational structure is unresolved, buried within the 0.2–0.4 Å width of each peak. The two bands on either side of the central one are due to residual vibrational population of modes not cooled efficiently in the supersonic expansion. Comparison with DIB data shows no interstellar absorption in this region. This is not surprising because the oscillator strength, ≈ 0.01 according to calculations, and a column density of $\sim 10^{11} \text{ cm}^{-2}$ would result in a DIB with an EW < 1 mÅ, i.e., hardly detectable.²⁹

The pattern of the components in the gas-phase spectrum of C_{18} mirrors some observations made on DIBs, though at different wavelengths.³⁰ The traces shown on the right of Figure 8 are two DIB recordings made with the same resolving power ($\approx 80\,000$). The traces shown on the right and the laboratory spectra at 100 or 20 K have similarities. Thus, it may be that large carbon

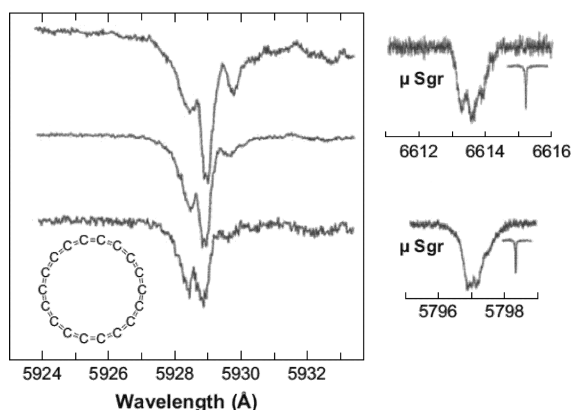


Figure 8. Origin band of lowest electronic transition of cyclic C_{18} measured in the gas-phase using a resonant two-photon ionization technique at a rotational temperature at ~ 100 K (top trace), 50 K (middle), and 20 K (bottom). On the right are shown two diffuse interstellar absorption features measured toward μ Sgr³⁰ at a comparable resolution as that for the laboratory C_{18} spectrum. Adapted with permission from ref 29. Copyright 2006 Institute of Physics.

rings with transitions at DIB wavelengths and much larger oscillator strengths than that of C_{18} could well be the carriers. The rotational profile would accommodate sizes up to a hundred carbon atoms and include the species with one or more hydrogen or heavier elements such as N or O. Ions are included and the selectivity would come from systems where the absorption falls in the DIB region and has a large transition moment like the C_{15} , C_{17} , ..., chains. Theoretical predictions of the appropriate systems is a necessity.

Comparison of laboratory spectra of C_7^- and NC_4N^+ with DIB data have been particularly intriguing. In the case of C_7^- , it was found that several of the transitions in the $A^2\Pi_u \leftarrow X^2\Pi_g$ electronic system measured in the laboratory either coincided with weaker DIB bands or were close, within 0.2 \AA .¹² Unambiguous spectroscopic agreement could not be obtained, as closer inspection of the data sets showed small wavelength and intensity

discrepancies.³¹ The case of the $A^2\Pi_g \leftarrow X^2\Pi_u$ absorption spectrum of NC_4N^+ is also striking.³² The measured rotational profile of the origin band is almost a mirror image of a double peaked DIB, shifted in wavelength by merely 1 \AA (Figure 9). These two examples show that, although the DIB absorptions cannot be of the isolated molecules in the gas-phase, the similarity in the patterns may lead one to contemplate if the species are on surfaces of grains. This would lead to a slight shift in the band positions and relative intensities.

The wavelength of allowed electronic transitions of carbon chains shifts systematically to the red with increasing size of the system. Thus, only a limited number of members of a homologous series will fall in the window of DIB observations. In the case of polyacetylene cations $HC_{2n}H^+$ ($n = 2-4$), the $A^2\Pi \leftarrow X^2\Pi$ origin bands lie in the this region. These have been measured in the gas-phase and compared to DIB observations.³² All results were negative, leading to upper limits of column densities of $<10^{12} \text{ cm}^{-2}$.³³ However, longer chains, $n = 4-6$, having the $A^2\Pi \leftarrow X^2\Pi$ transition in the near-infrared, would have excitations to higher electronic states in the visible region.³⁴ The fwhm of the absorption bands of higher electronic transitions have been measured to be $0.1-5 \text{ \AA}$, corresponding to lifetimes of $50-0.2 \text{ ps}$. For example, for $n = 4,5$ the origin band of the $B^2\Pi \leftarrow X^2\Pi$ transition lying in the DIB region has a width of $\sim 1.5 \text{ \AA}$ and an oscillator strength $f \approx 0.02$ comparable to that of $A^2\Pi \leftarrow X^2\Pi$. As this width is similar to many DIBs, this indicates that higher excited states for longer neutral and ionic species should be considered.³⁴

The situation concerning C_{60}^+ also remains unsettled. The electronic absorption spectrum of C_{60}^+ was obtained in a neon matrix at 6 K using the setup shown in Figure 1. The origin band at 9645 \AA and a vibrationally excited transition near 9400 \AA are apparent (Figure 10). The bands show solid state effects: phonon broadening and a splitting, which may be site structure or the presence of two geometric forms trapped in a neon matrix resulting from Jahn–Teller distortion affecting the degenerate ground state.³⁵ Thus, a priori, it is not evident what the shape of the bands will be in the gas-phase at low temperatures, in addition to the gas-matrix shift. Nevertheless, the laboratory absorptions

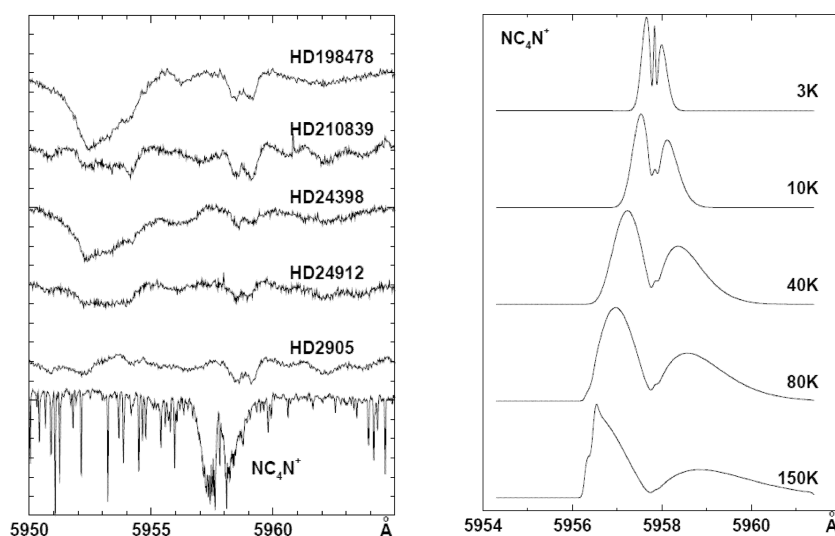


Figure 9. Left: origin band of the $A^2\Pi_g \leftarrow X^2\Pi_u$ transition of NC_4N^+ measured in the laboratory at ~ 80 K (bottom trace) compared to interstellar absorptions toward the indicated reddened stars. Right: change in the rotational contour as the temperature is increased from 3 to 150 K. The line width of the rotational lines is taken as 0.1 \AA , being representative of the velocity dispersion in diffuse clouds. Adapted with permission from ref 32. Copyright 2000 Institute of Physics.

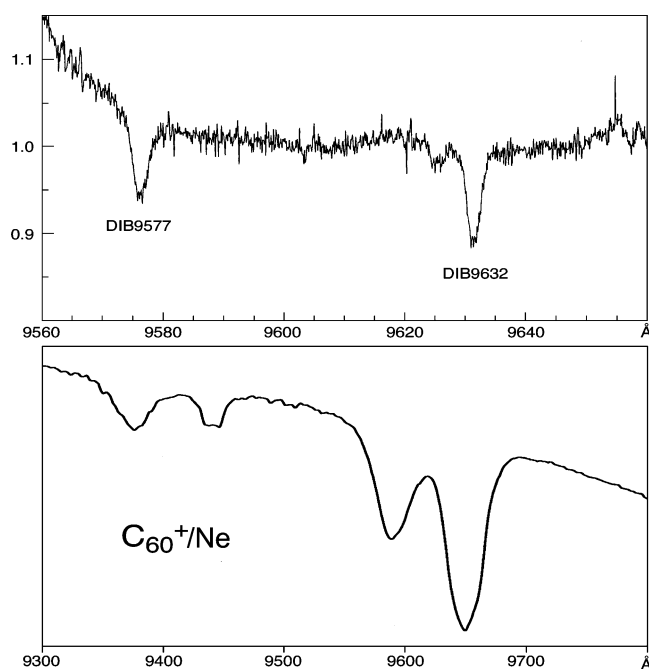


Figure 10. Comparison of the ${}^2E_{1g}-X^2A_{1u}$ electronic transition of C_{60}^+ measured in a 6 K neon matrix⁴⁵ with DIB absorption features. Adapted with permission from ref 35. Copyright 1994 Nature Publishing Group.

were compared to DIB measurements³⁵ in this region and the authors proposed that the interstellar absorptions are due to C_{60}^+ . The two sets of data are shown in Figure 10. It will require a gas-phase spectrum of C_{60}^+ at temperatures of 10–100 K to confirm this. This is particularly of current interest in view of the detection of neutral C_{60} in a planetary nebula via its IR transitions.³⁶ Experimental efforts to obtain the gas-phase spectrum of C_{60}^+ are in progress, using an ion trap.³⁷

An alternative approach to identify the carriers of the DIBs has been to use different mixtures in the discharge to produce reactive species containing carbon and hydrogen. The absorptions ensuing can be detected using cavity ringdown in the manner depicted in Figure 3. One can then compare any absorption observed with the DIB catalogues and, provided that a match is found, consequently try to identify the carrier. So far such studies have been made dominantly with carbon hydrogen mixtures. An example of this is shown in Figure 11, using acetylene diluted with

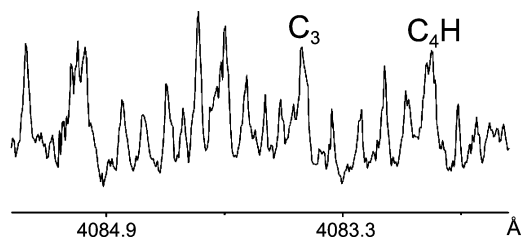


Figure 11. Absorption spectrum recorded by cavity ringdown using a pulsed discharge source with acetylene seeded in helium. Some absorptions of C_3 ($A^1\Pi_u-X^1\Sigma_g^+$) and C_4H ($B^2\Pi_u-X^2\Sigma^+$) are indicated.

helium in the discharge. Several absorptions are seen due to the concomitant production of several species. Only a few are identified, e.g., in this region some are due to C_3 and C_4H .

Among such scans, one broad absorption, centered on 5440 Å, was observed to match in position and width a broad DIB.³⁸

Initially the laboratory studies did not identify the molecule causing the absorption except that it contained just carbon and hydrogen. Subsequent investigation identified the absorption as the 4_0^1 transition of the $B^1B_1-X^1A_1$ electronic transition of C_3H_2 .³⁸ This could be proven first by measurements of the absorption spectrum (Figure 12) in neon matrixes using mass-

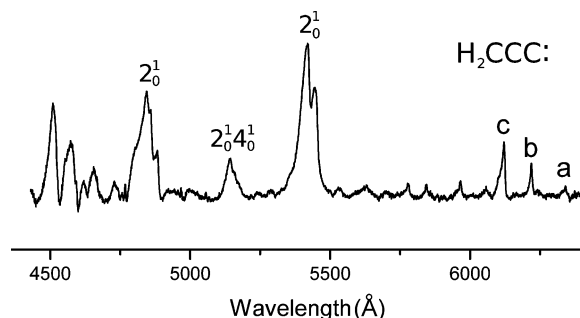


Figure 12. $B^1B_1-X^1A_1$ electronic absorption spectrum of $l-C_3H_2$ in a 6 K neon matrix was recorded using mass-selected deposition of $C_3H_2^+$. The bands a, b, and c were also observed by gas-phase measurements and rotationally resolved.^{40,41}

selected $C_3H_2^+$ ions with the setup of Figure 1. The same spectrum was obtained earlier by preparing $l-C_3H_2$ in a neon matrix via photolysis of a precursor.³⁹ Then the absorption at 5440 Å was again observed in the gas phase by cavity ringdown spectroscopy, the best signals being obtained in a discharge through allene in helium carrier gas. The intensity of this absorption correlates with the rotationally resolved ${}^1A_2-X^1A_1$ bands of $l-C_3H_2$, identified unequivocally earlier by the spectral analysis.^{40,41}

On the basis of the absorption seen in a neon matrix (Figure 12), the next member of the progression 4_0^2 in the $B^1B_1-X^1A_1$ band system of $l-C_3H_2$ was expected to be of similar intensity. Subsequently this was observed in the gas-phase, with a maximum at 4880 Å and a 40 Å fwhm about the same as for the 5440 Å band. The broadness of the 4_0^1 and 4_0^2 bands is a result of intramolecular processes, quite likely leading to isomerization, resulting in excited state lifetimes of ~ 100 fs. Such broad DIBs appear to be seen, though they require background correction and deconvolution of overlapping stellar absorptions.³⁸ Because two broad absorptions observed in the laboratory due to $l-C_3H_2$ coincided in wavelength and width with two broad DIBs, it was concluded that $l-C_3H_2$ is the carrier of the 5440 Å DIB. The assignment of this 5440 Å absorption to $l-C_3H_2$ in the laboratory is corroborated by the measurement of the photoelectron spectrum of $l-C_3H_2^-$ and theoretical modeling of the vibrational pattern.⁴²

A problem arises concerning the evaluated interstellar column density of $l-C_3H_2$, assuming that it is responsible for the whole 5450 Å DIB absorption. Using the calculated oscillator strength and Franck–Condon factors for the vibrational transition, the column density of $l-C_3H_2$ in the diffuse clouds where the 5450 Å DIB is observed would be $\sim 3 \times 10^{14} \text{ cm}^{-2}$.³⁸ This is much higher than expected because species such as C_3 have column densities in the same or similar clouds 2 orders of magnitude lower. On this basis, the assignment of the 5450 Å DIB to $l-C_3H_2$ has been questioned.⁴³ A recent mm-wave study attempting to detect $l-C_3H_2$ by its rotational transitions in the diffuse medium^{23,44} substantiates this point of view, as it shows that the column density would be less than 10^{11} cm^{-2} . Thus, the conclusion now has to be that, while $l-C_3H_2$ is present in diffuse clouds and it does

have an absorption at 5450 Å, the main intensity of the 5450 Å DIB is coming from the absorption of another species, which happens to have a comparably broad absorption at this wavelength but with a much higher oscillator strength than that of $I\text{-C}_3\text{H}_2$.

4. OUTLOOK

It took over two decades to obtain in the laboratory the gas phase electronic spectra of smaller neutral, cationic, and anionic carbon chains, and of their derivatives with hydrogen and/or nitrogen. The choice of the species for the investigations was based on the fact that they would have allowed transitions in the visible region and in relation to the identifications made by radio-astronomy in dense interstellar clouds. The results are that species comprising up to a dozen of carbon atoms cannot be carriers of the stronger DIBs. As pointed out, the molecules detected in the dense clouds, e.g., C_3H and C_6H , will undoubtedly also be present in the diffuse clouds, but their expected column densities together with typical oscillator strengths of the order of 10^{-2} imply that the DIB absorptions will be in the mÅ range and thus buried in the noise of current astronomical measurements.

However, the comparison of the laboratory and astronomical data indicate that a number of systems remain viable DIB candidates and that their laboratory electronic spectra are needed. One such set is of linear carbon chains comprising an odd number of atoms, C_{2n+1} $n > 7$. These molecules have very strong electronic transitions in the DIB region, and even modest column densities of 10^{11} cm^{-2} would lead to DIBs with an EW of 0.1 Å. Current attempts to measure these use ps pump–probe methods with subsequent mass-selection of ions. Initial success has led to the observations of the electronic transitions of the linear chains $\text{C}_6\text{--C}_9$. The absorption spectra are broad and indicate excited electronic state lifetimes in the ps range. An unknown still remains whether the linear species C_{17} , C_{19} , ..., with large oscillator strengths and transitions above 430 nm will have lifetimes longer than ~ 100 fs to be compatible with the widths of the stronger DIBs.

Also of relevance is the observation that the rotational profile of cyclic species comprising only carbon, e.g., C_{18} , are rather similar to DIB observations made, though at other wavelengths. The implication of this is that cyclic species with up to a hundred carbon atoms should also be investigated in the gas-phase, though a preselection must be made; they have to have absorptions in the DIB range, and one would seek those with a large oscillator strength, along the lines of the odd carbon chains. These can include the derivatives containing H, N, O, and their ions. It is too daunting of a task to study in the laboratory many such systems; theory could contribute to guide experimentalists as to which particular systems one should focus on in the laboratory.

Another project is to obtain the electronic spectrum of C_{60}^+ in the gas-phase at low temperatures. The absorption bands around 9645 Å measured in neon matrixes 20 years ago⁴⁵ remain the basis for the suggestion that these correspond to DIB absorptions.³⁵ For measurements in the gas-phase, the techniques of confining the C_{60}^+ ions in a radiofrequency trap while the internal degrees of freedom are relaxed to temperatures in the 10–30 K range by collisions with cryogenic helium are chosen. It has been demonstrated that electronic spectra at these low temperatures can be obtained, for species as large as the linear polyacetylene cation, HC_{16}H^+ , using excitation–dissociation spectroscopy.³³ However, the approach used a two-color scheme, which is not expected to work generally for large ions as fast

intramolecular processes of the excited electronic states tend to dominate. Alternative schemes are being developed.

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Notes

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Biographies

Corey A. Rice grew up in Bunker Hill, IL, and studied chemistry at Southern Illinois University Edwardsville where he obtained B.A. and M.Sc. in 2001 and 2004, respectively. He received a Ph.D. in physical chemistry from the University of Göttingen in 2007 under the supervision of Martin A. Suhm. Shortly thereafter, he joined the group of John P. Maier as a postdoctoral fellow, where he has worked on several projects including ion trapping and laser spectroscopy.



John P. Maier obtained a B.Sc. at the University of Nottingham, U.K., and subsequently a D.Phil. in physical chemistry from the University of Oxford in 1972, under the supervision of D. W. Turner. Since then he has spent his academic career at University of Basel, being appointed to the Chair of Physical Chemistry in 1992. In 1999, he was elected Fellow of the Royal Society, London. His research activity over the decades has been focused at the development and use of approaches to obtain for the first time the electronic spectra of radicals and ions, especially those of astrophysical interest.

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