The optical spectroscopy of extraterrestrial molecules

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The ongoing quest to identify molecules in the interstellar medium by their electronic spectra in the visible region is reviewed. Identification of molecular absorption is described in the context of the elucidation of the carriers of the unidentified diffuse interstellar bands while molecular emission is discussed with reference to the unidentified Red Rectangle bands. The experimental techniques employed in undertaking studies on the optical spectroscopy of extraterrestrial molecules are described and critiqued in the context of their application.

1. INTRODUCTION

As the last embers of a red giant star die down, it undergoes a series of expansions and contractions, puffing away the outer layers of the star, resulting in the expulsion of its carbon rich atmosphere into the cosmos. As the central stellar core contracts under gravity into a white dwarf, the atmosphere evolves into a nascent proto-planetary nebula, rich in carbon, oxygen, nitrogen (Fig. 1). Such a dignified end to the life of an intermediate mass star, such as our own Sun is in sharp contrast to the violent end encountered by higher mass stars \textsuperscript{1} which end their lives in supernova explosions. A supernova is triggered when the collapsing stellar core is too massive to be supported, against gravitational collapse, by electron degeneracy pressure (\textit{i.e.} the Pauli exclusion principle, as is the case in a white dwarf star). The resulting violent nuclear explosion heats the surrounding interstellar medium, through a variety of mechanisms, to temperatures in excess of $10^6 - 10^8$ K, sufficiently hot to generate X-ray emission. Elements from all over the periodic table are ejected into the cosmos: the atoms to be later incorporated into molecular clouds and future solar systems. All elements heavier than Fe are formed in supernovae.

The chemistry of interstellar space is different to that performed in a conical flask. It is slow, it is driven by ion-molecule and neutral-radical reactions in the gas phase \textsuperscript{1} and on the surfaces of dust grains, and it is highly exotic. The harsh radiation field in interstellar environments is also of great importance. There are a number of chemical models of interstellar space. Of note are the “UMIST gas-phase chemical network” of Millar and co-workers in Manchester \textsuperscript{2} and the “New Standard Model” of Herbst and co-workers in Columbus (NSM) \textsuperscript{3}. Both these models use complicated networks of kinetic equations to model the chemistry of various interstellar environments. However, these models may only be tested by spectroscopic observation of the relative abundances of interstellar molecules, which is a field

\textsuperscript{1}The mass limit above which electron degeneracy pressure cannot support a stellar core against the relentless crushing force of gravity was first derived by S. Chandrasekhar, for which he was later awarded a Nobel prize. Above 1.44 Solar masses a stellar core will collapse to a neutron star or black hole, resulting in a supernova explosion rather than the formation of planetary nebular. Precursor stars with masses in excess of 1.44 Solar masses may still avoid ending their lives as supernova if enough mass is lost from the star, during it’s late evolutionary stages, to prevent the remaining core mass exceeding the Chandrasekhar limit.
unto itself. Also, the numerous (thousands of) rate constants are being constantly updated with better experimental and *ab initio* results.

To understand the chemistry of interstellar clouds one must begin by first identifying the molecules therein. It is a great challenge posed by Nature to remotely identify the menagerie of molecules extant in the interstellar medium (ISM).

![Planetary Nebulae](image)

**FIG. 1** Planetary nebulae as imaged by the Hubble Space Telescope and the Anglo-Australian Telescope. Planetary nebulae are gas clouds surrounding stars typically hundreds of light years away. They take their name from their appearance when imaged in small telescopes, whereby they resemble gas giant planets from our solar system such as Uranus or Neptune. There is no association between planetary nebular and planets beyond this appearance.

Molecules are identified in the interstellar regions by their spectroscopic signatures in the millimetre, infrared and optical regions of the electromagnetic spectrum. While it is the millimetre region which has most greatly illuminated our understanding of the structures of interstellar molecules, this technique is blind to a family of molecules of interest: those without permanent dipole moments. For this reason, the UMIST and NSM models concentrate on reproducing the observed abundances of polar molecules 2, 3. An up-to-date list of molecules known to exist in the interstellar regions is given in Table 1 5.

In the following paragraphs, work concerning the identification of extraterrestrial molecules in various wavelength regimes is outlined. The astronomical facilities exemplified are done so in an Australian context, where possible, and so are not necessarily indicative of those facilities globally.

1.1. The millimetre-wave region. Molecules are heated by gravitational collapse, converting potential energy to kinetic energy which is distributed among the degrees of freedom of the constituent species. This energy can be radiated back into space by molecules as visible, infrared or millimetre-wave radiation. Molecules with permanent dipole moments, upon relaxation, radiate in the millimetre-wave region of the spectrum by cascading down the ladder of energy levels which describe molecular rotation. This radiation
is collected and analyzed to produce a forest of sharp, well-defined spectral lines. These lines are matched to rotational spectra observed in laboratory experiments and in doing so the extraterrestrial species are identified. Molecules with larger dipole moments are easier to observe by this technique and as such asymmetric carbon chains are a dominant motif in the list of known molecules from the interstellar regions.

Millimetre-wave spectroscopy is performed on extraterrestrial objects by so-called radio telescopes. Excellent examples of this type of instrument are the 64 m Parkes radio telescope, the 22 m Mopra telescope, and the Australia Telescope Compact Array, all administered by the Australia Telescope National Facility of the CSIRO 6 (Fig. 2). There are many groups who undertake laboratory experiments to which astronomical observations may be compared. In the laboratory, rotational spectroscopy is performed by a fourier-transform technique whereby the rotational spectrum is obtained in a similar fashion to the free-induction decay well known in the field of nuclear magnetic resonance. The group of Thaddeus and co-workers have discovered over fifty molecules of astrophysical relevance 7.

1.2. The infrared region. The infrared region features emission corresponding to vibrational relaxation of specific functional groups and bonds comprising interstellar molecules. Of note is the 3.3 µm emission lines which are thought to originate from polycyclic aromatic hydrocarbons (PAHs), such as naphthalene, anthracene and phenanthrene. Spectroscopy in the infrared is difficult, however, due to the interference of sources of background infrared emission (sky and telescope). Some regions of the infrared are “off-limits” to astronomers due to absorption of radiation by water in the atmosphere. Emission in the far infrared has been used to identify interstellar C$_3$ 23 and C$_5$ 22.

Due to technical difficulties associated with ground-based observations in the infrared, last year (2003), a new satellite was launched by NASA. This new instrument, SPITZER, (Fig. 2) is capable
of performing infrared spectroscopy in the wavelength region spanning 3-180\(\mu m\) at various levels of resolution. The ground-based Michelle (Mid-Infrared Echelle spectrograph) mounted on Gemini North, Hawaii, is capable of spectroscopy in the 7-26\(\mu m\) region with resolution of 30000\(^2\). The Anglo-Australian Telescope (AAT) at Coonabarabran is capable of spectroscopy in the 0.9-2.5\(\mu m\) range with resolution of 2400.\(^{10}\)

In the laboratory, infrared spectroscopy is routinely performed using a fourier-transform technique (FTIR). However, this technique is less sensitive than tunable diode laser spectroscopy (TDL). TDL spectroscopy as an absorption technique has been applied to the IR spectroscopy of many carbon chains and rings of astrophysical relevance. Of particular note is the Cologne Carbon Cluster experiment\(^{11}\) of Winnewisser and co-workers.

FIG. 2  Astronomical instruments used to observe extraterrestrial molecules. Top to bottom: Parkes radio-telescope; Australia Telescope Compact Array; Spitzer; Hubble Space Telescope; AAT at Coonabarabran; Gemini North (CFH in background).

1.3. The optical region.  It is in the optical regions of the electromagnetic spectrum (300-950\(nm\)) that there is much to be done. Despite the optical region being the part of the electromagnetic spectrum

\[ \frac{2R}{\lambda} = \frac{\lambda}{\Delta \lambda} \]
originally accessed by astronomers, there have been scarce new identifications of interstellar molecules by their electronic spectra. Examples of astronomical instruments available in Australia that access this region for the purposes of optical spectroscopy are the ultra-high resolution facility (UHRF) \((R \sim 900,000)\) and the University College London Coudé Echelle Spectrograph (UCLES) on the AAT. Facilities with Australian access include the Gemini Multi-Object Spectrograph (GMOS) on Gemini North (Hawaii) and South (Chile), which is a low resolution optical spectrograph. The Bench-mounted High Resolution Optical Spectrograph (bHROS) on Gemini South will be in routine operation shortly.

Molecules without permanent dipole moments may not be observed by millimetre wave spectroscopy, and those without infrared active vibrational modes cannot be observed by spectroscopy in that region. For instance, \(\text{C}_2\) may only be observed by optical spectroscopy. For these reasons, spectroscopy in the optical region offers possibilities for observing new interstellar molecules. This review focusses on the research being undertaken in the field of the identification of new interstellar molecules through their electronic spectra in the near-infrared, visible and ultraviolet spectrum.

The article is arranged as follows. Firstly, the absorption of starlight by molecules is discussed and astronomical and laboratory work in this area is reviewed in the context of the unidentified “Diffuse Interstellar Bands” (DIBs). Molecular emission is discussed in relation to the Red Rectangle paradigm and ongoing work in this area. The experimental techniques and results involved in performing interstellar spectroscopy in the laboratory are reviewed in the context of their application. Finally, state-of-the-art experiments are described and suggestions are made as to the future directions of the field.

2. MOLECULAR ABSORPTION - THE DIFFUSE INTERSTELLAR BANDS

The spectrum of light from many stars is well described to first order by black-body radiation theory: the hotter the star, the bluer its spectrum. So-called “reddened” stars are those for which the blue part of the spectrum is attenuated by scattering. The scattering takes place in the interstellar clouds, along the line of sight to the background star. The passage of the starlight though such a cloud can leave the signature of the DIBs imprinted on the stellar spectrum. With starlight as a “white-light” source, the interstellar cloud as a sample, and with spectrographs on Earth, one has all the essential elements of a benchtop spectrophotometer (albeit slightly larger).

Molecular clouds vary in their density. The denser clouds greatly diminish the brightness of the background star thereby also sheltering the interior of the cloud from harmful deep ultraviolet radiation. The denser clouds naturally have higher abundances of molecular species, which are measured by “column density”. Column density is an effective number of molecules in a column of space between the observer and the light source, typically quoted as having a 1 cm\(^2\) cross-section.

The spectra of many diatomic molecules have been known for decades. Diatomic species, such as \(\text{CH}, \text{C}_2, \text{CN}, \text{and CH}^+\), have been detected toward a number of clouds. Their column densities are regarded as standards with which chemical models of interstellar clouds may be compared. Less is known about absorption in the optical region by polyatomic molecules.

In the spectra taken towards diffuse clouds, there are approximately 300 absorption features of unknown origin. These features, collectively known as the “Diffuse Interstellar Bands” (DIBs), vary in width from 0.1-3 nm and cover the entire visible and near IR regions. There is a vast body of phenomenology pertaining to the identity of the DIB carriers, which has been reviewed elsewhere. There are various hypotheses as to which types of transitions are responsible for the DIBs. These are outlined below.

2.1. The carbon chain hypothesis. Carbon chains were first proposed as the carriers of the DIBs by Douglas. That the DIB absorbers are carbon chains is predicated upon the observation that carbon chains can exhibit very strong transitions in the visible region, and that they are known to exist
in molecular clouds. The list in Table 1 demonstrates that carbon chains are a widely exhibited motif of the known interstellar molecules. The carbon chains observed by millimetre-wave astronomy are necessarily strongly polar \( (e.g., H - C \equiv C - C \equiv C - C \equiv C - C \equiv C - C \equiv C - N) \) yet it is expected that the bare carbon chains \( (C_n) \) will also be present in molecular clouds. It is hypothesised that some or all of the DIB absorbers are carbon chain molecules.

The hypothesis is easy to prove, at least in principle. One must measure the absorption spectra of target molecules, in the gas phase, under isolated conditions, and compare these to astronomical spectra. An example of a positive identification of an interstellar carbon chain by this method is the observation of \( C_3 \) in interstellar clouds. \( C_3 \) had been previously identified in the laboratory and its spectrum at 405 nm was well known from laser-induced fluorescence spectroscopy and comets.

A survey towards \( \zeta \)-Ophiuchi, 20-Aquilae and \( \zeta \)-Persei revealed absorption by the \( A^1\Pi_u \leftarrow X^1\Sigma^+_g \) transition of \( C_3 \). The rotational profile was fitted to 80K and the column density was determined to be \( 1 - 2 \times 10^{12} \text{ cm}^{-2} \) (Fig. 3). Since then, \( C_3 \) has been observed towards many stars with column densities reported up to \( 10^{13} \text{ cm}^{-2} \). A strong relationship between the column densities of \( C_2 \) and \( C_3 \) with \( N(C_2)/N(C_3) \approx 40 \) has been reported. So far, searches for \( C_4 \) and \( C_5 \) by optical spectroscopy have been unsuccessful. Upper bounds have been placed on column densities of \( C_4 \) and \( C_5 \) towards \( \zeta \)-Ophiuchi of \( 10^{13} \text{ cm}^{-2} \) and \( 2 \times 10^{11} \text{ cm}^{-2} \) respectively. The value of \( N(C_4) \) relies on a calculated oscillator strength and is therefore less certain. It should be pointed out that \( C_5 \) and \( C_3 \) have been observed by high resolution IR absorption spectroscopy in carbon-rich nebulae. Carbon chains, bare, monohydrogenated or dihydrogenated are expected or have been shown to exist in the ISM. Whether they are the DIB absorbers can be rigorously tested by a combination of laboratory spectroscopy and observation. A large part of the work reviewed here was performed in Basel, Switzerland, in the group of J.P. Maier.

2.1.1. Resonant 2-Colour 2-Photon Ionization (R2C2PI) spectroscopy. The spectra of dihydrogenated chains, \( \text{HC}_n\text{H} \), were first observed in solution and in solid matrices. The gas-phase spectra of the even
series, HC$_{2n}$H, were recorded only recently. The spectra of HC$_{2n}$H ($n = 8–13$) were obtained by Resonant 2-Colour 2-Photon Ionization (R2C2PI) spectroscopy in a molecular beam produced by a discharge of diacetylene in argon. R2C2PI spectroscopy is a type of Resonance-Enhanced Multi-Photon Ionization (REMPI) spectroscopy. In such an experiment, the gas-phase supersonically cooled products of the discharge (containing C$_n$H$_m$ species with $n \geq m$) are irradiated by two laser beams. The first is scanned in wavelength. If a photon from the first laser is absorbed, then absorption from the second laser will overcome the ionization potential of the molecule and nascent ions will be produced. The ions are accelerated towards a detector, arriving at a time-of-flight (TOF) characteristic of the mass to charge ratio of the ion (generally speaking only singly charged molecules are observed). This experiment yielded the spectra of the even chains up to HC$_{26}$H, none of which were observed to lie in the visible region (the longest chain, HC$_{26}$H, absorbs at 340 nm). The reason for this behaviour is bond length alternation. The hydrogen end-caps of the chain induce triple-bond/single-bond alternation which slowly decays toward the molecular centre. The overall effect is that of the chain exhibiting a bandgap, which slows the movement of the absorption positions to lower energies as the chain length is increased. Very weak, forbidden, bands of the HC$_{2n}$H series have been observed in the visible region, yet these are not of relevance to astrophysical studies due to their low oscillator strengths.

FIG. 4  In R2C2PI spectroscopy, supersonically cooled molecules are ionized in two steps by photons of two colours (top-left) and then mass-analyzed. The energy of $\lambda_2$ is not energetic enough to ionize the ground state molecule in a one photon process, so appreciable ion signal is only observed when $\lambda_1$ is resonant with an excited state of the molecule. As the wavelength $\lambda_1$ is scanned, an excitation spectrum is produced. The mass spectrum of a hydrocarbon discharge appears as indicated in the top-right of the figure. When $\lambda_1$ is resonant, a mass peak will be enhanced by orders of magnitude in strength.

2.1.2. Cavity Ringdown Spectroscopy (CRDS). Absorption spectra of the odd chains HC$_{2n+1}$H ($n = 3–6$) were observed in the visible region by cavity ringdown spectroscopy (CRDS). CRDS can be
performed using pulsed lasers \(^{29,30}\) or continuous wave lasers \(^{28}\). The principle is as follows (see Fig. 5). Molecules are expanded into a vacuum chamber such that they cool supersonically. In experiments related to carbon chains, the molecules expanded into the vacuum are the products of a hydrocarbon discharge, much like the R2C2PI experiments outlined above \(^{28}\). The free jet expands in an optical cavity defined by two highly reflective mirrors mounted on either side of the vacuum chamber. A laser beam is injected into the cavity (tuned to support the particular wavelength). The decay of the light pulse in the cavity, as observed by a photodetector mounted exterior to the vacuum chamber, can be related to the reflectivity of the mirrors, and absorption of laser light by some molecular species extant in the free jet expansion. Scanning the laser beam produces spectra which must be analysed by the rotational structure, for there is no mass information about the absorber (unlike R2C2PI spectroscopy). Nevertheless, the spectra of \(\text{HC}_{2n+1} \text{H} \quad (n = 3 - 6)\) in the visible region were recorded in this way \(^{27}\). These spectra were not found to match any DIBs.

A simple free electron model of the electronic structure showed that the oscillator strength for these visible transitions increased with chain length. High-level MRCI calculations and CASSCF calculations did not support this assertion \(^{31-33}\). It was found by computation that the excited states of the \(\text{HC}_{2n+1} \text{H}\) series could be described by an admixture of two determinants. The determinants combined in even and odd combination to produce a lower energy excited state which carried very little oscillator strength and a higher energy state which carried a very large oscillator strength. The lower energy \(\tilde{A}\) states, represented by absorption of \(\text{HC}_{2n+1} \text{H} \quad (n = 3 - 6)\) in the visible region were thus found to be irrelevant to the DIB problem, on account of their vanishing oscillator strengths. This realization spurred a search for the \(\tilde{B}\) states by R2C2PI spectroscopy. Two bands were observed, for \(\text{HC}_{13} \text{H}\) and \(\text{HC}_{19} \text{H}\), both lying in the UV region \(^{33}\). It is concluded that dihydrogenated chains cannot be responsible for DIBs unless they are considerably longer than \(\text{HC}_{19} \text{H}\) (it is estimated that \(\text{HC}_{30} \text{H}\) will absorb in the visible region).

Due to their strong dipole moment, the monohydrogenated chains, \(\text{C}_{2n} \text{H}\), have been observed in the ISM by rotational spectroscopy \(^7\). The optical spectra of monohydrogenated chains have been observed in the visible region by CRDS and R2C2PI spectroscopy \(^{34,35}\). That the spectra did not match any known DIBs places upper limits on their column densities of \(\approx 10^{12} \text{cm}^{-2}\). The optical transitions observed for the \(\text{C}_{2n} \text{H}\) chains do not have large oscillator strengths. In general, polarization of the carbon chain reduces the overlap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, thereby reducing the possible oscillator strength of the transition.

Of the bare carbon chains, \(\text{C}_3\) and \(\text{C}_5\) have been observed in the interstellar medium \(^{17,22,23}\). The absorption by \(\text{C}_3\) towards \(\zeta\)-Oph is due to a relatively weak perpendicular transition, first observed in fluorescence in comet tails. There is a much stronger parallel transition of \(\text{C}_3\) in the vacuum ultraviolet region \(^{38}\). This strong parallel transition is seen analogously in all \(\text{C}_{2n+1}\) chains. The oscillator strength grows with the size of the chain and the wavelength shifts linearly (as opposed to \(\text{HC}_{2n} \text{H}\) which exhibits a band gap). The absorption spectra of \(\text{C}_7\) to \(\text{C}_{21}\) have been observed in a neon matrix \(^{36,37}\). Absorptions due to the strong parallel transition all lie in the visible region yet gas phase spectra, with which astronomical observations may be compared, have so far proved elusive. It is the authors’ opinion that a carbon cluster source coupled to the R2C2PI technique represents the best chance of observing these spectra in the laboratory.

Gas-phase spectra of the even carbon chains have also proved elusive. Condensed phase spectra of several members of the \(\text{C}_{2n}\) series have been observed \(^{39,40}\). The transitions observed often lie in the visible region and thus these molecules cannot be ruled out as the DIB carriers. Definitive proof, one way or the other, will come with unambiguous gas-phase spectra.

Open shell carbon chains are not the best candidates as DIB absorbers, as their transitions are highly mixed, either distributing oscillator strength across many transitions or shifting the oscillator strength into the UV for medium length chains. Of the closed shell chains, there are \(\text{HC}_{2n} \text{H}\), \(\text{HC}_{2n+1}^{+}\).
and $C_{2n+1}$. As noted above, the polyyne series, HC$_{2n}$H, suffers from a non-linear dependence of absorption wavelength with chain size. The gas-phase spectrum of HC$_{26}$H lies in the near UV and only much longer chains will begin to absorb in the visible ($2n \sim 40$). Of the HC$_{2n+1}^+$ cations, not much is known. Their spectra should mimic the $C_{2n+1}$ neutrals however the transitions will not be quite so strong since the overlap between the highest occupied and the lowest unoccupied molecular orbital is reduced in the polar molecules.

2.1.3. Photodetachment spectroscopy. It would be remiss not to discuss the possibility of carbon chain anions in the ISM. Indeed, carbon chains have been found to possess very high electron affinities. In particular, polar carbon chains may be efficient at electron capture due to the existence of dipole-bound states. The spectrum of C$_7^-$ was observed to match very closely several DIBs. More precise observation showed that the match was not exact, and as such C$_7^-$ was not responsible for any DIBs. The spectra of anions are recorded in the gas phase is a similar manner to R2C2PI spectra. The set-up is illustrated in Fig. 6. Anions are produced in a hydrocarbon discharge and accelerated in a time of flight (TOF) tube to the laser interaction region. The mass-selected anion bunch is intercepted by a pair of laser beams which cooperatively excite the anion and subsequently photodetach an electron. The nascent neutral molecules are oblivious to the ion mirror which reflects the remaining anions. The neutrals impacting onto the MCP at 2.7 keV induce a signal due to production of secondary electrons. The neutral signal as a function of the first laser pulse yields the excitation spectrum of the anion.

While the possibilities are numerous, the outstanding candidates as carbon chain carriers of the DIBs are the odd-numbered carbon chains. It is expected that this hypothesis will be tested within the next few years. The examples of carbon chains terminated with heteratoms are too numerous to review here. However, they have been observed in molecular clouds (see Table 1) and are likely important species in interstellar chemistry.

2.2. The PAH hypothesis. Polycyclic aromatic hydrocarbons (PAHS) are a class of molecule characterized by conjoined “benzene ring” moieties. They may be thought of as fragments of graphite with hydrogens bound to the edge. Examples of PAHs are naphthalene, anthracene (see Fig. 9).

The presence of PAHs in the ISM was first proposed in the context of their possible role in the form of the UV extinction curve. The suggestion that PAHs might be the carriers of the DIBs came later, with the realization that in order that smaller PAHs absorb in the visible they should be in cationic form.

With the “coming of age” of Mid-IR astronomy, particularly results from the European Space Agency (ESA) Infrared Space Observatory (ISO) mission such as the identification of interstellar benzene, PAH molecules have been interpreted as the natural carriers for the observed Mid-IR emission band. Indeed, recent work has seen the first indications that the Mid-IR emission features can be well fitted by composites of emission from numerous PAH species. Unfortunately, the composite nature of the Mid-IR bands makes this region of the spectrum poor for identification of specific PAH molecules. The promising possibilities of using Far-IR emission bands (vibrational frequencies associated with the bending of the skeletal structure of molecules) to uniquely identify PAH molecules has been discussed.

Further support for the PAH origin of DIBs comes from their spectral stability (with respect to environmental variations in the excitation spectrum). While the Mid-IR PAH features are observed to vary greatly in structure and intensity ratios between observations, the DIBs are observed to be surprisingly uniform in structure, with only the relative intensity of different bands altering with sight line, presumably an effect of differing abundances of species along different sight line. It has been demonstrated that environmental effects are significant in altering the emission profiles of the Mid-IR
FIG. 5  In cavity ringdown spectroscopy (CRDS), supersonically cooled molecules are injected into an optical cavity in a vacuum chamber. The decay profile of the laser pulse as observed by a photodetector exterior to the cavity is modulated by absorption by molecular species. The modulation of the decay profile as a function of laser wavelength yields CRDS spectra.

PAH features. This can account for the large variations seen in the observed Mid-IR emission and the discrepant intensity ratios when compared with laboratory observations. However, it has been shown that this is not the case for visible light PAH transitions. They show that PAH absorption features would be observed to be stable, at the level of current observations, over an extreme range of environmental conditions.

Circumstantial evidence in favor of larger molecular carbon species is reported whereby a potential “carbon-crisis” is highlighted: insufficient carbon is identified in ISM to support the proposed build up of carbon rich dust grains. High molecular weight PAH molecules could act as repositories for carbon. It has been estimated that up to 20% of cosmic carbon in the Galaxy is contained in PAHs yet more likely it is less than this. The current status of possible matches between DIBs and laboratory PAH features has been reviewed. With the presence of PAH molecules in the ISM now widely accepted, the search for transitions in the visible region which could give rise to the DIBs is a logical next step. This is a problem for laboratory astrochemistry.

Since most neutral PAHs amenable to spectroscopic study absorb only in the UV, research has concentrated on measuring the spectra of the PAH cations in the visible region. Until recently, only matrix isolation spectra of PAH cations were available. The first gas phase spectrum of a PAH cation was measured by resonance enhanced dissociation spectroscopy of naphthalene cation, Np⁺. The spectrum produced was noisy and not definitive. It was not until 1999 that the absorption spectrum of the naphthalene cation (the smallest PAH) was recorded. Two bands were recorded by CRDS.
FIG. 6 An illustration of the apparatus used to produce the spectra of carbon chain anions. Anions are produced in a discharge and then accelerated in a time-of-flight (TOF) tube. The mass-selected ion bunch is intercepted by a pair of laser pulses which cooperatively neutralize the anion. The neutral signal as a function of $\lambda_1$ is the photodetachment spectrum.

*(vide supra)* in a pulsed discharge source. Following this, the entire spectrum of the Np$^+$ cation was produced using an action spectroscopy technique pioneered earlier in work on benzene analogs 65. Np$^+$ was clustered with argon “spectator atoms”. The cluster mass distribution as measured by time-of-flight mass spectrometry was observed to change when energy was absorbed by the cationic chromophore. Essentially, the spectator atom is evaporated when the Np$^+$ chromophore absorbs a visible photon, and the mass change is recorded. The “action” as a function of wavelength yields a proxy excitation spectrum. This technique is powerful however suffers from the spectator atoms inducing slight changes in the electronic chromophore. The change (0.1 nm at 648 nm) is enough to exclude these spectra from being directly comparable to astronomical observation. More recently, acephenene and naphthalene cations have been studied in more detail by CRDS 66. The technique which yielded the first PAH excitation spectrum, namely resonance-enhanced multiphoton dissociation (REMPD) has undergone a small revival. The development of ion-traps had led to the ability to irradiate a population of ions with multiple photons, thereby accumulating signal before detection. Mass-selected ions are trapped in the gas phase and irradiated with several laser shots. Mass spectrometry of the fragments reveals acetylene loss as an indicator of the ions having absorbed energy. The probability of the ion having absorbed enough to break carbon-carbon bonds is greatly enhanced if the first photon may be absorbed in such a way as to place the ion in an excited state. In this way, warm gas phase spectra of naphthalene and anthracene have been recorded 67. Mounting an ion trap on a cold head is one way of alleviating the problems of temperature on the spectrum 68.

At the time of writing, not one PAH, neutral or cationic, has been identified in the ISM by optical spectroscopy. Indeed, not one DIB carrier has been positively identified. While it is certain that PAHs
exist in the ISM, it is unclear whether they should be dominantly ionized or neutral. As PAHs are likely to have large electron affinities, there is also scope for the existence of PAH anions in the ISM. Indeed, the electron affinities of some carbon-based molecules exceed the ionization energy of alkaline earth atoms. As such, in an environment where one finds sodium atoms, one may also find carbonaceous anions. It is also unclear as to whether the PAHs should be wholly intact. One conclusion that may be drawn from the observed PAH cation spectra is that they are most probably not responsible for narrow DIBs, because the PAH cation bands observed thus far are all very broad (≈10Å), presumably due to lifetime effects associated with internal conversion processes. The Possibilities regarding extensions of the PAH hypothesis will be discussed below.

2.3. Something completely different?. There have been many suggestions over the years as to the identity of the DIB absorbers. Those suggestions taken most seriously, namely carbon chains and PAHs, have been discussed above. The remaining candidates are plentiful, and only need be tested in the laboratory.

The possible existence of buckminsterfullerenes in space was first suggested by Kroto 69. That C$_{60}$ in particular is so symmetrical and so stable lends credence to the hypothesis. However, the strongest absorptions of C$_{60}$ occur in the UV and as such this molecule is not responsible for any DIBs 70.

Following the publication of the matrix isolation spectrum of the C$_{60}^+$ cation 71, a search was carried out towards a number of stars which revealed two new DIBs. The DIBs were found to have a spacing and absorption wavelength consistent with the observed spectrum of C$_{60}^{+}$ in an argon matrix. While the assignment of the DIBs observed near 9500Å to C$_{60}^{+}$ seems entirely reasonable, definitive proof can only come by the laboratory gas phase spectrum of C$_{60}^{+}$, which has so far proved elusive. C$_{60}^{2+}$ may also exist in appreciable concentrations in the ISM, since the second ionization potential of C$_{60}$ is extraordinarily low (11.4 eV) 73.

The column density of H$_2$ in molecular clouds is approximately $10^6$ times greater than that of the most abundant polyatomic carbon species. This implies that for a given oscillator strength of a transition, only one millionth of the H$_2$ present need be in a particular state to effect the same absorption as other proposed carriers of the DIBs. Indeed, there exist inter-Rydberg transitions of H$_2$ calculated to match DIBs very well 74, 75. Experimental observations of the inter-Rydberg transitions have revealed intriguing properties of H$_2$ such as “outer well” states with W-shaped potential energy curves 76, 77. Another theory put forward attributes the DIBs to Rydberg matter 78, aggregations of excited atoms and molecules bonded through electrostatic interactions of Rydberg electrons.

The existence of interstellar diamonds was suggested in 1969 79. They have since been shown to exist as nanometre sized crystallites in carbonaceous meteorites 80. Given the ability for defects and surface effects to produce colour centres, nanodiamonds present themselves as possible candidates as the carriers of some of the DIBs.

3. MOLECULAR EMISSION - THE RED RECTANGLE

The search for molecules in Space by optical spectroscopy may be performed by the molecules’ absorption or emission of visible and UV light. The search for molecules by absorption is intrinsically linked to the search for the DIB carriers. In the case of C$_3$, the molecule was first observed by emission in comet tails, subsequently in the laboratory and then finally by absorption in interstellar clouds 17.

The “Red Rectangle” (see Fig 7) is a biconical proto-planetary nebula. In the case of the Red Rectangle, the core is a binary system. One of the stars has come to the end of its life and has started puffing off its atmosphere to leave behind a white dwarf. The other component is a helium white dwarf which died previously in a similar manner. It will have been more massive, leading to an earlier evolution.
The “Red Rectangle”, a nearby proto-planetary nebula, is a carbon-rich object in which there are unidentified emitters, thought to be molecular. Much of its mass will most likely have been accreted onto the other star, rather than puffed off in a previous nebula. The system will evolve into a binary white dwarf system.

The unusual geometry of the nebula is not entirely understood. The Red Rectangle exhibits a “bipolar flow” which carries mass away from the central stars into the interstellar medium. It is suggested that the central stars give rise to a pair of jets that precess about one another (like a spinning top). The nebula’s emission is also unusual: it displays a number of unidentified emission lines, the so-called Red Rectangle Bands (RRBs). These bands, occurring in the visible region are speculated to be due to unusual carbon containing molecules. There is also suggestion that at least one of the features is related to a DIB. Thus, identification of the carrier of the band may be a “foot in the door” to the identification of the DIB carriers. This feature is illustrated in Fig. 8.

The advantage of looking for molecules in emission is that the species necessarily fluoresce, or phosphoresce. In the case of fluorescence, the carriers may be observed by laser induced fluorescence (LIF) spectroscopy, so long as the species can be created in the laboratory. One possible problem is that the LIF spectrum of a hydrocarbon discharge may be too rich to positively identify individual species. However, there has been much progress in the last five years in diagnosing the products of a hydrocarbon discharge by gas-phase spectroscopy. It is now possible that much of the fluorescence can be assigned. The remainder will belong to new molecules. Identification of mass-unresolved spectra will come about by a combination of ab initio theory, isotopic studies, and rotational structure. In this way a molecular carrier at 443 nm was very recently identified as C$_5$H$_5$.

It has been suggested that some of the RRBs are due to $\tilde{a}^3\Pi_u \rightarrow \tilde{X}^1\Sigma_g^+$ phosphorescence of C$_3$ (which has never been observed in the gas phase). Indeed, CO is seen in the Red Rectangle due to its phosphorescence: the so-called Cameron Bands (between 1850 and 2600 Å). If the species corresponding to the molecular carrier of the RRBs is produced in a hydrocarbon discharge, but the emission observed is due to phosphorescence, then it is likely that the molecules will pass out of the light collection region and into the vacuum pump before emitting a detectable number of photons (phosphorescence typically occurs on the ms time-scale, and molecular beams move at about 1mm/µs). An experiment designed to circumvent this problem is described in section 4.

In Fig. 8, the observed spectrum of one of the RRBs is displayed alongside a simulated spectrum performed by the authors. The seemingly convincing simulation was performed with $A'' = 0.84 \text{cm}^{-1}$ and $A' = 0.76 \text{cm}^{-1}$. Such a change of rotational constant (10%) upon excitation is unusual yet not unheard of. One class of molecule with $A$ constants very sensitive to excited state are the carbenes.
These molecules possess lone-pair electrons which, when excited, bring about large changes in geometry and thus rotational constant \( s \). A rotational constant in the range given is slightly unusual. It is too large to be due to three collinear second period atoms, so must be accounted for by an effective diatomic (or some other slightly non-collinear structure \( s \)). Candidates include radical molecules such as those observed in discharges by R2C2PI spectroscopy \( s \), \( s \) and rotational spectroscopy \( s \). Of these, \( C_7H_3 \) has a structure which has calculated rotational constants in the ground state consistent with the observed spectrum.

\[ \begin{align*}
A'' &= 0.84 \text{ cm}^{-1}, \\
A' &= 0.76 \text{ cm}^{-1}, \\
B &= C = 0.05 \text{ cm}^{-1}
\end{align*} \]

![Wavelength (Å) vs. Rotational Constants](image)

**FIG. 8** A high resolution portion of the extended red emission of the Red Rectangle as compared to a simulation.

4. **UNDER CONSTRUCTION: WHERE TO FROM HERE?**

The identification of extraterrestrial molecules in the optical region can occur in two ways. Either the spectrum is recorded firstly in the laboratory and subsequently in an extraterrestrial object, or the absorption or emission line is observed by astronomy and subsequently in the laboratory. Neither approach has been particularly successful. A search for \( C_5 \), which we know to exist in the ISM \( 2 \), at...
optical wavelengths, was unsuccessful. It was concluded that the column density was only one order of magnitude too low for optical detection. However, a search for lines which might match \( C_{60}^+ \) turned up two promising features. Unfortunately, the gas-phase optical spectrum of \( C_{60}^+ \) is unknown and thus this identification required confirmation. As described above, there are hundreds of unidentified absorption and emission features in astronomical spectra. Identifying these is a job for laboratory spectroscopy. Many avenues have been explored, including a host of carbon chain species and PAH cations. New experiments, presently under construction, are described below.

![Structures of cations](image)

**FIG. 9** Structures of cations thought to exist in the interstellar medium. Clockwise from top-left: naphthalenylium cation, phenanthrenylium cation, anthracenylium cation and buckminsterfullerenylium cation (\( C_{60}^+ \)).

### 4.1. Spectroscopy of exotic cations

Cation spectroscopy is difficult. They possess a much higher density of states than neutral species and as such often have efficient internal conversion pathways. As a consequence, only small cations fluoresce. LIF is thus of limited applicability. Direct absorption measurements by CRDS are possible. However, the species must have a density in the free-jet expansion above a threshold limit for detection. This technique is also mass-unresolved and thus identification of a band carrier is often not straightforward. R2C2PI spectroscopy is currently only applied to neutral species, but in principle could be applied to cations if the mass-to-charge ratio can be changed in a resonant process. Since a single ion can be detected, this technique does not suffer from the problems of sensitivity which plagues CRDS. Cations are difficult to doubly ionize. As they are already charged, removal of an extra electron is approximately twice as difficult as the first. The most amenable example may be \( C_{60}^+ \). The ionization potential of \( C_{60} \) is 7.62 eV, and that of \( C_{60}^+ \) is 11.4 eV (109 nm). These photon energies required are only just becoming convenient. Another problem is the internal conversion
mechanisms which preclude LIF from being applied to cations. A consequence of internal conversion is that the double ionization step must occur from the electronic ground state. Signal will be very sensitive to the photon energy of the second laser pulse. One unexplored direction is the implementation of ultrafast lasers for ionization (τ_{FWHM} ≈ 100fs). The ionization laser need not be high-resolution (and necessarily are not due to the time-energy uncertainty principle). One advantage of ultrafast laser pulses is that their wavelength can be changed by non-linear optical techniques with high efficiency (due to the high peak-power). Thus, deep UV wavelengths may be accessed more easily than with nanosecond laser pulses. The ionization step may also be effected by multiphoton processes, which might be called resonant 2-colour multi-photon double-ionization spectroscopy (R2CMPDI).

One problem of C_{60}^+, and for large cations in general, is that they are difficult to place into the gas phase and they are difficult to cool to temperatures comparable to the interstellar medium. One solution is to trap the ions and cool them with a buffer gas. In this way, it is possible to load an ion trap with mass-selected C_{60}^+ or another large cationic species and then cool to 5 K or higher with a helium buffer. Spectroscopy is then performed in the trap. This may be done either by R2CMPDI, or by REMPD as in Ref. 67.

Mass selection prior to trapping opens up the possibility of performing spectroscopy on derivatives of PAH cations. It has been observed by one of the authors (TWS), that nascent hydrocarbon cations produced in a R2C2PI experiment will readily absorb photons of energy ≈ 6 eV and shed hydrogen atoms. In this way, the signal observed for C_{9}H_{3}^+ also yielded the same resonance enhanced ion signal at the masses for C_{9}H_{2}^+, C_{9}H^+ and C_{5}^+. It is thus likely that, in the interstellar medium, PAH cations will absorb UV photons and shed hydrogen atoms. This process will be in equilibrium with a hydrogen capture process (ion-atom reaction) and it is possible that the derivatized population of PAH cations and neutrals will be significant. It is worth noting that a mono-dehydrogenated PAH neutral will have a π-electronic structure similar to its cation and will likely absorb in the visible. Obvious candidates for these studies are naphthalenylum and anthracenylum cations and the corresponding neutrals.

4.2. Phosphorescence spectroscopy. Fluorescence spectroscopy is performed by observing the emission, by molecules, of photons at the point of laser-molecule interaction. Where the emission lifetime is much longer than ns-µs, the emission cannot be observed in this way. For this reason, relatively little is known of laser-induced phosphorescence (LIP) spectroscopy, and indeed about forbidden transitions in exotic molecules.

It has been speculated that the RRBs may be due to phosphorescence. While it is unlikely that forbidden transitions play any part in the DIBs, if a molecule is formed in a triplet state by some reactive mechanism, the radiative lifetime is irrelevant: molecules experience long delays between collisions in the rarefied environments of molecular clouds and nebulae (10 to 10,000 s).

One way to observe phosphorescence in the laboratory is to excite a forbidden transition in the gas-phase with a powerful laser, then freeze the triplet excited molecules onto a substrate at 5 K. The ensuing phosphorescence is then detected at leisure as the molecules are now frozen into a matrix of the carrier gas (e.g. argon). Phosphorescence as a function of laser wavelength yields a gas-phase phosphorescence spectrum which may be compared to astronomical spectra. This technique has already been applied to the spectroscopy of benzaldehyde.

5. CONCLUDING REMARKS

Models of interstellar chemistry are not only tested by predicting observations of column densities by millimetre-wave spectroscopy, but must also predict abundances of species without permanent dipole moments to which millimetre-wave spectroscopy is blind. The identification of molecules in the optical region
of the electromagnetic spectrum requires high resolution astronomical observation coupled with sophisticated laboratory experiments. While astronomical observations have uncovered hundreds of unidentified and presumably molecular absorption and emission features, and laboratory spectroscopy has produced cold, gas-phase spectra of hundreds of candidate carriers, there is as of yet not one certain match between a DIB or RRB and a laboratory spectrum. C$_3$ has been observed in molecular clouds, but so far C$_5$ has been elusive in the optical region.

As far as identification of the DIBs is concerned, the outstanding candidates within the frame of the carbon chain hypothesis are the odd numbered pure carbon clusters. These chains possess strong transitions which increase linearly with the size of the chain. They are also known to absorb in the visible region. Other candidates yet to be tested are the iso-electronic monohydrogenated carbon chain cations. These are only now being studied in the condensed phase. Gas-phase spectroscopy of cations is a field under development. The coming years should see some progress. An outstanding yet unobserved spectrum is that of C$_{60}^+$ in the gas-phase. This spectrum, when obtained, will confirm whether or not this cation is abundant in the interstellar medium. Modeling its formation should be a great challenge for theoretical astrochemists.

The spectroscopy of PAHs in the laboratory is ongoing business. Very few gas-phase spectra of PAH cations and derivatives have been observed. More studies are needed before an informed opinion can be formed on the importance of PAHs with respect to the DIBs. One of the great challenges facing these studies is the methodology with which the spectra of cations may be observed in the gas-phase.

The RRBs remain unidentified. It is clear that the carrier emits, and as such it will be observed in the laboratory by observation of its laser-induced emission. The challenge to the experimentalist is to build the laser-induced fluorescence/phosphorescence apparatus and find a way of making the presumably exotic carrier in situ. The carrier must be abundant in the Red Rectangle nebula and thus should be produced in a discharge of the right precursor mixture. Whether the carrier possesses a heteroatom remains to be seen.

The identification of molecules in the interstellar medium is an on-going quest. The coming decade should see the identification of several of the DIBs, or if not, then certainly the gas-phase spectra of troublesome cations will be obtained. On this quest, physical chemists and astronomers walk together in an example of cooperation and collaboration between two seemingly different fields of scientific endeavour.

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