Author: Bacalla, X.
Title: Electronic spectroscopy of molecules of astrophysical interest
Issue Date: 2019-07-02

Chapter 1

Introduction

ESO / Adhemar M. Duro Jr.

The motion of stars and other celestial bodies along the sky has long been used by our ancestors as an indicator of change. Careful tracking of these objects enabled agricultural societies to know, for instance, when it was best to sow seeds for a bountiful harvest. They have served as beacons for navigating on both land and sea. Apart from keeping time and direction, they have also been associated with the divine and were consulted for guiding various forms of human activity. Charting the position of celestial objects has, in many ways, put us in our place in the cosmos. And in the span of recorded history, this has been the whole deal of the study of astronomy.

A major break from the tradition of 'positional' astronomy came in the early 1800s, lead by Willam Hyde Wollaston and Joseph von Fraunhofer. They took notice of the dark lines that appear in the spectrum of the sun[1] and cataloged them systematically. Soon thereafter, scientists began to incorporate prisms into their telescopes and pointed these instruments towards other stars which also showed dark lines in their spectra as well as towards the moon and the planets. In the laboratory, various chemicals were burned and the light they gave off was examined through similar prisms that produced unique emission features. With their invention of the spectroscope and an improved flame source around the 1860s, Gustav Kirchhoff and Robert Bunsen were able to deduce a correspondence between the spectrum produced by the flame of burning specific substances and the dark lines found in the solar spectrum—uncovering the material composition of the sun. This development gave rise to a new analytical technique, known as spectroscopy, applicable to atoms and molecules, which has revolutionized the way how astronomy is practiced and has essentially added another set of eyes to the human observer.

Spectrochemical analysis relies on the premise that different substances carry unique spectral signatures. Through the spectroscope, a [hot and] glowing object will produce a continuous spectrum of colors whose intensity is defined by its temperature. A flame will produce bright lines in its emission spectrum with colors (measured in terms of the wavelength of light) which are characteristic of the burning chemical. Likewise, substances such as gases may absorb certain wavelengths from a light source and leave out specific dark lines, producing an absorption spectrum. In the context of astronomical spectroscopy, a star is one example of such light source which produces a combination of a continuous spectrum masked with the absorption (and, in some cases, emission) features from the gases in its atmosphere.[2] Besides identifying chemical composition, spectroscopy can also be used for determining the star's motion along the line-of-sight, known as its radial velocity. In accordance with the Doppler effect, the absorption lines of a star will shift to longer (red) or shorter (blue) wavelengths depending on whether the star is moving away or towards the observer. For instance, a gravitationally-bound (i.e., mutually orbiting) star system having radial velocity components will exhibit spectral features that oscillate over time along the wavelength scale. With this the spectral signatures of the stars can be discriminated from any other that comes from some intervening material along the sightline. It was through this method that further evidence was found for the existence of an 'interstellar medium', instigated in 1904 by Johannes Hartmann with his discovery of a stationary calcium absorption line in the spectrum of the multiple star system δ Orionis (Mintaka).

---

[1] Prior to 19th-century Europe, it was already known that sunlight, when passed through a prism, disperses into a band of colors commonly known as a 'spectrum' (*pl.* spectra), as seen in a rainbow. In the solar spectrum the features that manifest as dark lines are actually missing colors.

[2] This has been the basis for the categorization of stars, from the Secchi classes to the Morgan-Keenan classification which is used as the standard today.

The interstellar medium. The interstellar medium (ISM) is an integral component of our galaxy which pervades the space in between the stars. Since the pioneering work of Hartmann, our knowledge of the ISM has significantly increased with the development of laboratory and astronomical instrumentation, and of [big] data handling and analysis. The ISM is now known to be composed of various environments that result from the close interplay among its main constituents of ordinary matter and [ultraviolet] radiation, cosmic rays (high-energy charged particles), and magnetic fields. A large fraction of its material composition is in the form of atomic and molecular gas (both neutral and ionized) which takes up the bulk of its total mass whereas only about 0.5–1% exists as tiny solid particles of silicate- and carbonaceous dust (Ferrière 2001). The ISM is further divided into generalized 'phases' which are based on the kinetic temperature T, number density n, and ionization state of hydrogen, being overwhelmingly abundant, in these interstellar environments (Table 1.1).

Table 1.1: Phases of the interstellar medium (Wooden et al. 2004, Snow & McCall 2006).

ISM component	common name	T [K]	n [cm^{-3}][a]	A_V[b]	H state[c]
Hot ionized	coronal gas	10^6	0.003		H^+
Warm ionized	diffuse ionized gas	10^4	> 10		H^+
Warm neutral	inter-cloud H I	10^3–10^4	0.1		H^0
Cold neutral					
Atomic	diffuse clouds	30–150	1–100	< 0.2	H^0
Molecular	diffuse clouds	30–100	100–500	~ 0.2–1	$H^0 + H_2$
	translucent clouds	15–50	500–5000	~ 1–5	H_2
	dense/dark clouds	10–50	10^4–10^6	> 5	H_2
Mol. hot cores	protostellar cores	100–300	$> 10^6$		H_2

[a] For molecular environments, n is the density of H_2.

[b] Extinction A_V is the absorption and scattering of light traversing through dust and gas particles. The higher the value, the more opaque the environment is to optical/visible wavelengths.

[c] Neutral atomic hydrogen is written as H, H^0, or H I, and its singly-ionized cation as H^+ or H II.

The predominant state of carbon in the cold medium also distinguishes each cloud type: C^+ in diffuse, C^0 in translucent, and CO in dense clouds (Snow & McCall 2006). This division into components, however, curtails the complexity of the ISM as the distribution of interstellar matter is rather continuous, with both rarefied and clumpy regions having no sharp boundary (i.e., exhibiting 'phase transition fronts'), and is far from homogeneous as different types of clouds could be present along a sightline or even coexist within a single structure. Thermal instability and turbulent processes cause the aggregation and mixing of material that lead to temperature and density fluctuations in the various phases. Nevertheless, the classification can be used for describing the thermodynamic conditions in localized areas of much larger, heterogeneous structures (Vázquez-Semadeni 2012).

As alluded to before, hydrogen constitutes a sizable portion (90.8% by number n, 70.4% by mass m) of the elemental composition of the ISM, followed by helium (9.1% n; 28.1% m), and trace amounts (0.12% n; 1.5% m) of heavier elements (labeled in astronomy as 'metals') such as oxygen, carbon, and nitrogen which exist in the gas phase and may well be locked up in dust grains; this partition is only slightly different to the 'cosmic composition' based on spectral measurements of the sun, stars, and meteorites (Ferrière 2001, Spitzer 1978 p.4). In the cores of the densest and coldest clumps of interstellar material, hydrogen becomes shielded from the ionizing and dissociating ultraviolet radiation of stars which allows for the formation of molecular hydrogen through H recombination on dust grain surfaces (Solomon & Wickramasinghe 1969, Carruthers 1970). Cosmic rays with sufficient energy can penetrate the interior of these clouds and produce ${H_2}^+$, H^+, and He^+; these ions react with abundant neutral species (e.g., CO, O, N, O_2, N_2) which trigger the synthesis of other ions and complex molecules (Herbst & Klemperer 1973, Smith 2011, Indriolo & McCall 2013). Equally important is the presence of icy mantles on interstellar solid particles that serve as catalytic sites and promote more complex molecule formation which would otherwise take time, if at all, to happen purely in the gas phase in these relatively dilute environments (Allen & Robinson 1977, Tielens & Hagen 1982, Herbst & van Dishoeck 2009, Linnartz et al. 2011, 2015, Öberg 2016). As these dark clouds become larger and denser, the inward self-gravity of the cloud overcomes its outward gas pressure which leads to gravitational collapse – sometimes set off by perturbing forces such as galactic tides or the shockwaves generated from the explosive death of a nearby star (supernova) – giving birth to new stars (Jog 1999). The same supernova provides energy and material enrichment to its surroundings, initiating chemical reactions and spewing out metals which further contribute to the molecular diversity in these interstellar regions. Thus, much more than just a substance where stars are embedded, the ISM also plays a significant role in the processes that govern star and planet formation and in the overall recycling of matter in our galaxy.

Currently circa 200 different molecules[3] (McGuire 2018) (excluding isotopologues) have been identified in the ISM or in circumstellar envelopes (i.e., the shell of material surrounding a star that is shed off as it evolves). These range from simple, diatomic species, with CH, CN, and CH^+ being the first molecules detected in space (Swings & Rosenfeld 1937, McKellar 1940, Adams 1941, Douglas & Herzberg 1942), to 'complex' molecules of six or more atoms, such as the c-C_2H_4O ring (Dickens et al. 1997), the first detected interstellar anion C_6H^- (McCarthy et al. 2006), the branched i-C_3H_7CN (Belloche et al. 2014), the chiral CH_3CHCH_2O (McGuire

---

[3] `https://cdms.astro.uni-koeln.de/classic/molecules` (accessed on 6 March 2019).

et al. 2016), the large fullerenes[4] C_{60} and C_{70} (Cami et al. 2010), and the $C_{60}{}^+$ cation (Berné et al. 2013). Inorganic (i.e., non-carbon-based) molecules have been found as well, like OH (Weinreb et al. 1963), H_2O (Cheung et al. 1969), NaCl (Cernicharo & Guèlin 1987), and ArH^+ (Barlow et al. 2013); however, all of the complex ones are organic, which is telling of the propensity of carbon to 'catenate' (or link with other C atoms to form a [branched] chain or ring) and the durability of its covalent bonds against the harsh environments of interstellar space. A large majority of these molecules are identified through their characteristic emission features typically at radio and submillimeter wavelengths, and a few are seen in absorption in the infrared (IR), optical/visible, and in the ultraviolet (UV) regions of the electromagnetic spectrum (Menten & Wyrowski 2011). Radio and, to a good extent, optical observations can be done from the ground whereas IR and UV detections largely require space-based telescopes which are free from telluric features[5] that severely contaminate astronomical spectra. Moreover, it should be noted that firm detections require a set of criteria (see e.g., Herbst & van Dishoeck 2009) and that there still exists a surplus of spectral signatures without a specific chemical (or 'carrier') attributed to them. These include the anomalous microwave emission (AME) (Kogut et al. 1996, Leitch et al. 1997), the unidentified infrared emission (UIE) (Russell et al. 1977, Bregman et al. 1983), the extended red emission (ERE) (Cohen et al. 1975, Furton & Witt 1992), and the 2175-Å UV bump in the interstellar extinction curve (Stecher 1965, Cardelli et al. 1989). But perhaps the most enduring of all the unknown features are the diffuse interstellar bands (DIBs)—an enigma that in December of this year (2019) will exactly be 100 years old.

The diffuse interstellar bands. The DIBs (Fig. 1.1) are some 500 absorption features that are observed in the line-of-sight to many stars, whose continuum emission is reddened due to interstellar dust and gas particles.[6] These features are broader, with full width at half maximum values of around 0.4–23 Å (2–120 cm^{-1}), compared to those produced by interstellar atomic species with FWHM less than 0.1 Å (Hobbs et al. 2009). Some of them (Fig. 1.2), primarily the stronger ones, can be approximated with a Lorentzian lineshape (Snow et al. 2002) or with multiple Gaussian functions (Sonnentrucker et al. 2018) while others have multifaceted structures resem-

---

[4] Fullerenes are a stable form of molecular carbon having a hollow, cage-like structure (C_{60}, also known as buckminsterfullerene or buckyball, has a shape of a truncated icosahedron, similar to that of a soccer ball) with carbon atoms at the vertices of each pentagonal- and hexagonal face.

[5] From the Latin *tellus*, or 'earth'. These are absorption features from the Earth's atmosphere.

[6] [Interstellar] reddening is a phenomenon caused by a predominant extinction of short-wavelength visible light which leaves over longer wavelengths and makes a glowing object appear redder than it actually is (related to the reddening of our sun during sunrise and sunset). This is quantified by comparing the object's observed and hypothetical/true color, known as the astronomical 'color excess' E_{B-V}.

bling the band profiles of molecules (Sarre et al. 1995, Galazutdinov et al. 2008). Indeed, the strongest bands first discovered appeared hazy on the edges when recorded using a photographic plate (hence the name 'diffuse') which reinforces the hypothesis that the DIB carriers have a molecular nature. DIBs can be found mostly in the cold neutral component of the ISM (diffuse and translucent clouds) and in extragalactic sources such as the Magellanic clouds (Ehrenfreund et al. 2002), the Andromeda galaxy (Cordiner et al. 2008), and in moderately redshifted ($z \sim 0.5$) objects (Junkkarinen et al. 2004). Some narrow DIBs also seem to converge to the wavelengths and structures of the emission bands seen towards the Red Rectangle nebula (Sarre 1991, van Winckel et al. 2002). Inter-DIB correlation is not strongly pronounced, if at all, (Moutou et al. 1999) which favors the 'one DIB, one carrier' hypothesis. On average, they tend to correspond with the amount of reddening, except for lines-of-sight through dense clouds where UV radiation is effectively shielded (also known as the 'skin-effect'); this observation implies that carrier formation is inhibited in dense cloud interiors and is only concentrated on the edges (Snow & Cohen 1974). Notwithstanding their weak correlation with each other, DIBs may be classified into families of species based on, for example, their intensity ratios among each other (Krelowski & Walker 1987, Cami et al. 1997) or their correlation with the column density of C_2 (Thorburn et al. 2003, Elyajouri et al. 2018). A number of DIBs have also been detected in the near-IR (Geballe et al. 2011, Cox et al. 2014), and much fewer in the UV (Watson 2001, Bhatt & Cami 2015). (For detailed DIB reviews, see also Herbig 1975, 1995, Sarre 2006, Cami & Cox 2014, and Geballe 2016.)

The identification of the DIB carriers has remained elusive for nearly a century now[7] since the discovery of the first two DIB features ($\lambda\lambda$5780 and 5797) around the early 1920s by Mary Lea Heger in her PhD work on interstellar sodium.[8] Around a decade after this serendipitous finding, Merrill (1934), Beals & Blanchet (1937), and Merrill & Wilson (1938), as part of a series of the first systematic investigations on DIBs in the 1930s, confirmed their interstellar nature based on how they remain fixed relative to the wavelength shifts of stellar lines caused by the orbital motion of a stellar binary (as was noticed by Heger) and how their absorption intensities scale generally with distance and amount of reddening (which implies that more of the interstellar material, including those that produce the DIBs, is being probed). Merrill & Wilson proposed micron-sized solid particles as the carrier, because it was already known that dust in interstellar clouds correlated with the reddening of background stars (Trumpler

---

[7] In 2015, the singly-ionized buckminsterfullerene cation ${C_{60}}^+$ was reported as a carrier of two near-IR DIBs ($\lambda\lambda$9577 and 9632, approximate central wavelengths in Å) (Campbell et al. 2015) and confirmed by observations using the Hubble Space Telescope (HST) (Cordiner et al. 2019).

[8] In 1919–1920, Heger measured the spectra of various binary stars, including ζ Persei and ρ Leonis where the two DIBs were seen the strongest. Although she focused primarily on the search for interstellar sodium lines, she was the first to record and notice these DIB features and had it published in 1922. (See McCall & Griffin 2013 for a thorough historical account.)

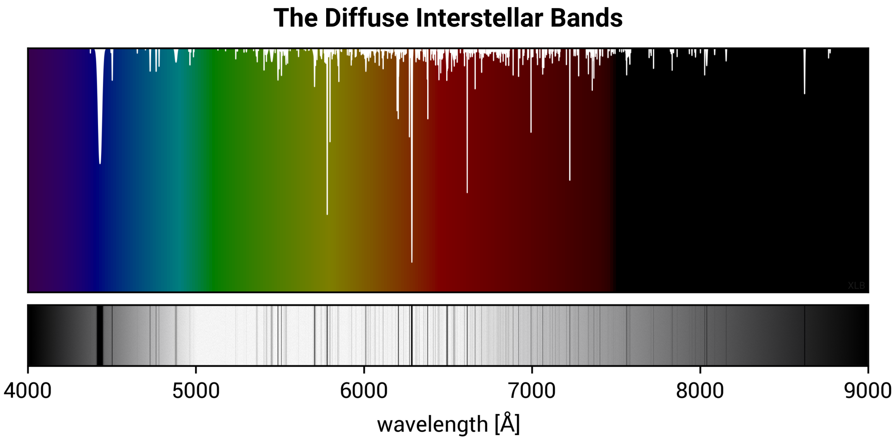


Figure 1.1: DIBs absorption spectrum towards HD 183143 (upper panel, white trace), simulated using band profile measurements from Hobbs et al. (2009). The bottom panel shows an approximation of how these features might have looked like on an exposed photographic plate detector, with the stellar lines removed. The 'near-IR DIBs', including the two attributed to C_{60}^{+} (Campbell et al. 2015, Kuhn et al. 2016, Cordiner et al. 2019), are not shown. Data available online: `http://dibdata.org/` (accessed on 26 June 2017).

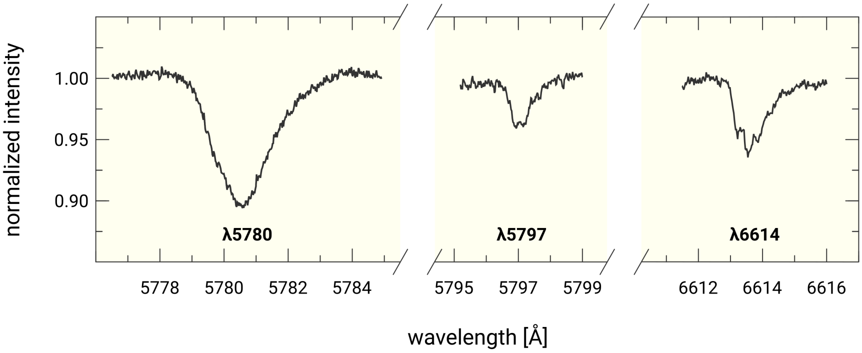


Figure 1.2: Examples of DIB features seen in the spectra toward HD 147165 (wavelength axes are spliced). Notice the difference of their band profiles and the presence of some fine structure, suggesting a molecular origin. *Figure adapted from* (Cox et al. 2017).

1930). Clouds containing dust grains that have partially aligned with the interstellar magnetic field contribute a linear and circular polarization to the background starlight (Hall 1949, Hiltner 1949, Davis & Greenstein 1951, Martin et al. 1972); however, no polarization is observed in the DIB features (Walker 1962, Greenberg & Stoeckly 1971, Cox et al. 2011), which is a strong argument against the dust carrier hypothesis. One of the other earlier suggestions were simple molecules, which was also stimulated by their recent discovery in the ISM at that time. Candidates such as CO_2, Na_2, O^-, C^-, solid O_2, metastable H_2 embedded in dust grains, ${CH_4}^+$, and NH_4 were put forward on the basis of near coincidences of available laboratory spectra to the DIB wavelengths or on theoretical considerations on the possible features that the molecules would produce (see e.g., Swings 1937, Saha 1937, McKellar 1960, Herbig 1963, and Herzberg 1967). Likewise, these early proposals did not survive as more results came out from the laboratory as well as from astronomical observations that, for instance, have constrained the interstellar chemical routes that dictate their abundances in these DIB environments. Molecular hydrogen, being an abundant molecule in the ISM, had led Sorokin & Glownia (1995) to propose highly-excited (Rydberg-state) H_2 as a possible carrier, which was complemented with laboratory work (Ubachs et al. 1997). It remains a challenge, however, to explain the spectroscopic processes necessary to produce these exotic species in the diffuse ISM (Sorokin et al. 1998, Holmlid 2004).

Overall, free (or unbound) molecules are among the strongest contenders for DIB carriers to date, in contrast to spectra produced in the solid phase which exhibit varying wavelength shifts. The broadness and shape of DIBs may be explained by unresolved lines due to the short lifetime of molecular excitation (e.g., through 'predissociation' or 'internal conversion') or as a result of unresolved rotational patterns. Attention was given to large molecular carriers after Danks & Lambert (1976) showed that certain spectral parameters for heavier species can be chosen to match the features of a couple of DIBs. For this, Douglas (1977) proposed as carriers the yet-to-be-detected (in the diffuse ISM) bare linear carbon chains of 5–15 atoms, as these would produce bands in the visible region[9] and would be protected from UV photodissociation through radiationless transitions between their energy states. Around this time, carbon chains of a different variety (cyanopolyynes and monohyrides / carbon chain radicals and ions) were also detected in dense clouds and circumstellar envelopes through their rotational transitions in (sub)millimeter and IR wavelengths. Experimental work to support Douglas' idea was initiated by Krätschmer (1986), albeit done with solid matrices which induced wavelength distortions. Subsequent studies employed similar matrix-isolation techniques together with time-of-flight mass spectroscopy to record the electronic spectra of these exotic molecules. Gas-phase laboratory spectra came later with the development of molecule production such as using hollow cathode discharges, supersonic plasma expansions, and electron-impact ionization sources that

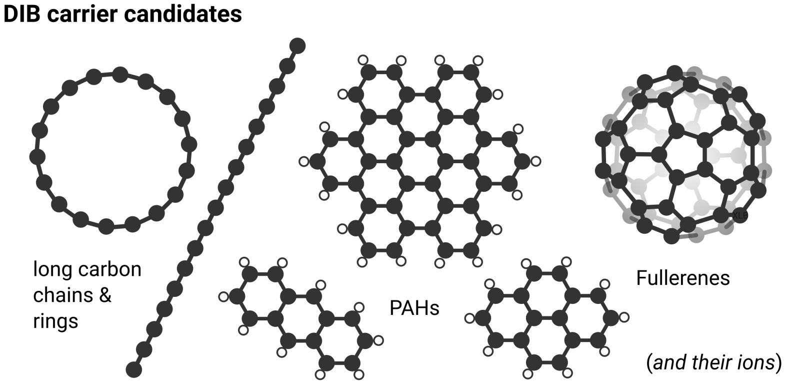
---

[9] As the molecule becomes larger (or longer, in the case of linear carbon chains), its (fundamental) electronic transitions situate to the red or at longer wavelengths.

were coupled with sensitive detection schemes, including, but not limited to, cavity ring-down (CRD), laser-induced fluorescence (LIF), and two-color resonant photodetachment spectroscopy. (See Nagarajan & Maier 2010 for a list of carbon chains that have been studied and the corresponding references.) This now allowed for a direct comparison of laboratory data on carbon chains to astronomical spectra, which resulted in many data that, in the end, were proven not to match DIB features. Notable examples of near identifications include the C_7^- anion (Tulej et al. 1998) with at least five bands coinciding with DIBs (this was dismissed through follow-up high-resolution astronomical observations by McCall et al. 2001), the NC_4N^+ cation with a rotational contour that looks similar but is slightly offset compared to the double-peaked λ5959 DIB (Motylewski et al. 2000), a then newly detected DIB at 5069 Å attributed to HC_4H^+ (Krełowski et al. 2010b) which was refuted by arguments on band profile mismatch (Maier et al. 2011b), and the l-C_3H_2 chain having two features coincident with the $\lambda\lambda$4881 and 5450 DIB (Maier et al. 2011a) which was quickly challenged for discrepancies in its band intensity ratio that yielded an anomalous abundance in comparison to what is derived from the DIBs themselves (Krełowski et al. 2011) and from its observed interstellar abundance (Liszt et al. 2012). These investigations have led to the conclusion that small chains containing ≤ 12 carbon atoms are not responsible for at least the strongest of the DIB features; longer bare carbon chains and rings still qualify as candidates (Jochnowitz & Maier 2008, Rice & Maier 2013).

Another class of organic molecules of interest are the polycyclic aromatic hydrocarbons (PAHs) which are made up of carbon atoms arranged in a honeycomb-like lattice that are terminated by hydrogen atoms on the edges. These molecules were first proposed as potential DIB carriers by van der Zwet & Allamandola (1985), Leger & d'Hendecourt (1985), and Crawford et al. (1985), owing to their tenacity to UV photodissociation and, consequently, their relative high abundance in the ISM as inferred from their 'collective' mid-IR emission (with Puget et al. 1985 and Allamandola et al. 1985 attributing the ubiquitous UIR bands to the PAHs), and for their ions to exhibit their 'species-specific' absorption features in the DIB wavelength range. Laboratory data in both the solid- and gas-phase are available (Salama et al. 1999, 2011, and references therein); however, this has not yielded a convincing match with the DIBs. Much of these individual PAH signatures are still being searched for in space in the visible and UV which also adds to the challenge of pinning down a unique PAH-DIB carrier. The detection of interstellar naphthalene ($C_{10}H_8{}^+$) and anthracene ($C_{14}H_{10}{}^+$) cations by Iglesias-Groth et al. (2008, 2010) towards one star was contested by Searles et al. (2011) and Galazutdinov et al. (2011) and remains an open issue.

Alongside the PAH-DIB hypothesis, the fullerene family (C_{60}, C_{70}, their ions and derivatives) is also considered as an attractive solution to the DIB mystery, being a stable configuration of carbon that is highly robust against photofragmentation (Kroto 1987, Leger et al. 1988, Kroto & Jura 1992). These carbon cages have been detected in space through their mid-IR emission in planetary nebulae and star-forming regions



(see e.g., Cami et al. 2010, Sellgren et al. 2010) and, much recently, in the diffuse ISM (Berné et al. 2017). Results from matrix experiments (Fulara et al. 1993a) had led Foing & Ehrenfreund (1994, 1997) to [inconclusively] attribute two bands of the $C_{60}{}^{+}$ cation to a then new pair of near-IR DIBs at $\lambda\lambda$9577 and 9632 on the basis of a comparably consistent band separation and intensity ratio. This finding was later confirmed by Campbell et al. (2015) using a helium atom-tagging technique that allowed for an extrapolation of the gas-phase electronic spectrum, in addition to finding three more absorption bands, of $C_{60}{}^{+}$ (Campbell et al. 2016a,b). A similarly indirect measurement using ultracold helium droplets corroborated the tagging experiment (Kuhn et al. 2016, Spieler et al. 2017). Follow-up astronomical observations have revealed DIBs corresponding to the newly recorded electronic bands (Walker et al. 2015, 2016), which were questioned (Galazutdinov et al. 2017, Galazutdinov & Krełowski 2017) and defended (Walker et al. 2017) on grounds of telluric pollution and inconsistent band intensity ratios. Clearly, more [space-based] observations are needed to settle the matter (Cordiner et al. 2017, Lallement et al. 2018). In the most recent HST study (Cordiner et al. 2019) it has been possible now to identify two of the weaker $C_{60}{}^{+}$ bands, besides the two already known stronger bands, and proof is accumulating that $C_{60}{}^{+}$ is indeed a DIB carrier. This does not explain, however, how such large species can form under the harsh conditions in the diffuse interstellar medium.

Other candidates have also been suggested based on calculated electronic transitions, such as tubular PAHs (carbon nanotubes) (Zhou et al. 2006), the CH_2CN^- anion (Cordiner & Sarre 2007), and proflavine and its ions (Bonaca & Bilalbegović 2010), which all still await confirmation from laboratory spectroscopy. The current consensus favoring carbon-based molecules (and setting aside the other candidates) has definitely benefited from the synergy of observational, experimental, theoretical, and computational work. As our knowledge of the DIBs broadens, the criteria become more stringent (see e.g., Snow 2014) for better constraining the seemingly overwhelming possibilities of molecular combinations and arrangements of potential DIB candidates.

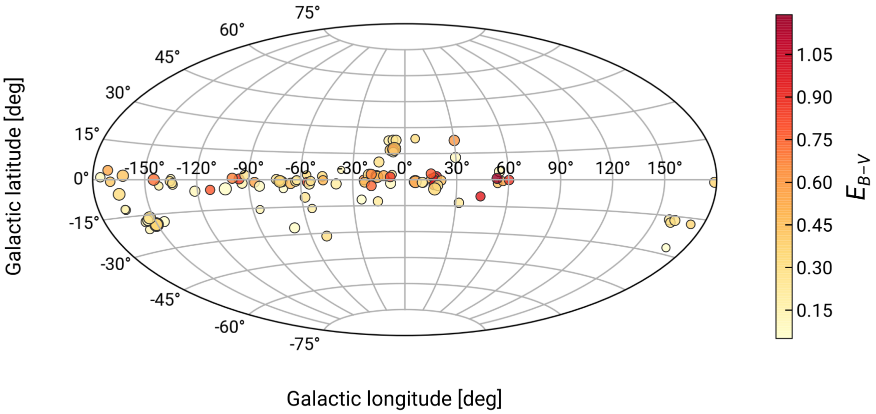


Figure 1.3: Distribution of EDIBLES sightlines in the Milky Way. The color spectrum corresponds to the reddening index (color excess) of the target star and the symbol size is determined by the total-to-selective extinction ratio R_V ($= A_V/E_{B-V}$; this parameter describes the dust grain size distribution along the sightline). *Figure adapted from* Cox et al. (2017).

The ESO Diffuse Interstellar Bands Large Exploration Survey (EDIBLES). It comes as no surprise that the total number of DIBs discovered rose markedly with the advancement of instrumentation (telescope optics, dispersion media, detection and recording means), offering a much higher signal-to-noise ratio and spectral resolution, as well as the implementation of accurate models for better telluric correction, especially that most of the research on DIBs is done using ground-based, optical telescopes. In the past half century or so, many sky surveys have been made not only to search for DIBs but also to determine how their behavior can be dictated by the physical and chemical properties of the environments where they are seen (or vice versa) to constrain, if not eventually identify, the carriers. Most of these were dedicated to either focus on a few of the strongest DIBs towards a large sample of sightlines (e.g., Friedman et al. 2010, Yuan & Liu 2012, Puspitarini et al. 2015), or to survey many DIBs in just a few targets (e.g., Jenniskens & Désert 1994, Hobbs et al. 2009). A relatively recent observational program called the European Southern Observatory (ESO)–Diffuse Interstellar Bands Large Exploration Survey (EDIBLES) was undertaken to complement these previous surveys, with the best of both worlds – studying many DIB features towards many sightlines – in order to better infer the [molecular] characteristics of the carriers by utilizing a statistically significant data set (Cox et al. 2017).

EDIBLES is a large (250+ hr) ‘filler’ program (ESO ID 194.C-0833, PI. N.L.J. Cox) using the Ultraviolet and Visible Echelle Spectrometer of the Very Large Telescope (VLT-UVES) in Paranal, Chile, implemented to observe the spectra of early-type (hot and bright) stars along the Galactic plane (Fig. 1.3) that probes the diffuse- and translucent ISM. (For more details and project goals, see Cox et al. 2017 and Cami et al. 2018.) A total of 123 unique sightlines are targeted and, as of April 2019, over 90% have been observed. To briefly summarize the survey design: four standard configurations of UVES (Dekker et al. 2000) are employed, with wavelength settings centered at 3460, 4370, 5640, and 8600 Å, covering from about 3042 to 10 420 Å. It offers a high spectral resolution of $\sim 70\,000$ ($\sim 100\,000$) in the blue (red) arm and a high signal-to-noise ratio (S/N) with a median value of around 500–1000. These specifications make EDIBLES a versatile data set to not only detect and study the DIBs but also to include other interstellar features such as C_2 and CN (and in particular, OH^+; Chap. 5 in this thesis) which can be used as additional diagnostics for the physical and chemical conditions (e.g., the Galactic cosmic-ray ionization rate) in the DIB environment.

★

It may well be haphazard to argue that telescopes ought to have more powerful optics for better light collection to detect more of the weak DIBs, and the spectrometers used in conjunction with them be of a much higher resolution than what is currently achievable; the technological demands involved for these improvements are quite *astronomical.* While this is undoubtedly important in knowing more about the DIBs and their carriers, high-sensitivity and high-resolution electronic spectroscopy in the laboratory provides us with accurate molecular parameters that we can use for modeling temperature-dependent band profiles, and inferring the presence of much weaker signatures to compare with (and even guide) astronomical observations.

Thesis contents

In the next chapters, I will present the results of my PhD work that revolves around the goal of understanding the DIB problem, involving laboratory spectroscopy and observational analysis.

Chapter 2 describes the experimental techniques that I have employed in recording spectra specific to the study of carbon-chain radicals. These are namely Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy (IBBCEAS) and Cavity Ring-Down Spectroscopy (CRDS). The two methods are used in a complementary fashion; combining the advantage of the fast data acquisition and wide wavelength coverage of IBBCEAS together with the high resolution of CRDS ensures an efficient search and identification of [new] spectral features that may be directly compared with astronomical DIB spectra. Details on the synthesis of molecules through hydrocarbon plasma expansions are also provided.

Chapters 3 and 4 focus on the hexatriynyl radical, C_6H and its heavier isotopologue, $^{13}C_6H$. The C_6H carbon chain was first found in space (Suzuki et al. 1986) before its spectra was even recorded in the laboratory (Pearson et al. 1988) using millimeter-wave spectroscopy. Despite failing the criteria for a DIB carrier, the electronic spectrum of this molecule is rich with information unraveled using high-resolution CRDS which can nevertheless provide insight on how, for instance, band profiles can change with subtle intramolecular interactions. In these contributions, the electronic origin band of $^{13}C_6H$ is reported for the first time, and an extensive energy level scheme for C_6H is formulated on the basis of rovibronic assignments and literature data (mm-wave, matrix isolation, and hollow-cathode spectra, ab-initio calculations, and isotopic substitution). Additionally, a Renner-Teller analysis is invoked to explain and assign the different electronic transitions.

Finally, in Chapter 5, electronic transitions of the hydroxyl cation OH^+ are searched for in astronomical spectra from the ESO Diffuse Interstellar Bands Large Exploration Survey (EDIBLES). The interstellar abundance of OH^+ is quantified and from this the rate of cosmic-ray ionization (CRI) in diffuse-translucent clouds is inferred. This quantity is especially important for modeling the chemical evolution of various interstellar species in these environments which may well include the molecular DIB carriers (see e.g., Lepp et al. 1988). It is found in this contribution that the rates are higher than what was previously derived through submillimeter, infrared, and UV observations. This is due to a revised formulation of the OH^+ abundance – CRI rate relation using updated oscillator strength values for the OH^+ transitions. It is possible, however, that these sightlines have inherently high concentrations of OH^+, and thus, lead to a high rate of CRI derived. Nevertheless, the results serve as a complementary check to other methods of deriving the CRI rate, using ground-based observations of multiple OH^+ transitions in the UV.