

# PART I

## OVERALL PROPERTIES OF THE DIFFUSE INTERSTELLAR BANDS

# Diffuse Interstellar Bands: Past and Present

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**Abstract.** The diffuse interstellar bands (DIBs) have come to the fore as an important mystery. This paper presents the history of DIB discovery and research; their importance; a summary of their properties; constraints on proposed identifications; a survey of DIB papers (including graduate student's theses); and a web site that lists DIBs paper from 1922 to 2011 (to be extended to the present).

**Keywords.** ISM: abundances, ISM: atoms, ISM: lines and bands, ISM: molecules

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## 1. Introduction

The diffuse interstellar bands (DIBs) have been a mystery since they were discovered almost a century ago. By chance, a young graduate student found two broad absorption bands in her spectra, taken for her research on binary stars. Later, other astronomers found that these bands were formed in the gas or dust in interstellar space.

At first DIBs were thought unimportant, a sidelight. No graduate student had the courage to write a thesis on DIBs because jobs were scarce (does that sound familiar?) so it was better to choose a non-controversial topic. Now things have changed. DIBs are seen as important: Ph.D. theses on DIBs are getting in vogue; see the list in Appendix A. Maybe one of these people (or their kids) will solve the mystery.

DIBs are *old*. When the first complex molecules formed in the history of the universe and the density of the gas permitted molecules to form, DIBs were a natural by-product. Current cosmological models say that stars, interstellar molecules, and galaxies, were formed about a billion years after the big bang. Maybe we can find DIBs in very red-shifted quasars.

One thing we can say is that more than one source is involved because of the many DIBs (more than 500) that are observed; one molecule can't do *everything*. In the worst case, every DIB has a different source: one DIB, one molecule.

There has been one past conference on DIBs. It was held in Boulder, in 1994, with Xander Tielens and I as co-chairmen of the organizing committee. The attendees numbered 64; now, in this conference, the number is 113. The Boulder meeting was not sponsored by the IAU; instead NASA contributed some money. The proceedings were published by Kluwer.

George Herbig has been a mainstay in DIBs research from 1963 until 2000, including a comprehensive DIB review paper (1995). A list of his DIB publications can be found in the DIBs archive (see the last section of this paper).

## 2. The importance of DIBs

We can say that DIBs represent the largest reservoir of organic material in the galaxy! That is a bold statement but it might be true, because all viable suggestions involve carbon. (Organic doesn't necessarily mean living it only means carbon is important in the molecules.)

Another sign of the growing importance of DIBs: you now get government grants to study them! This is fairly new. Before the 2000s people had to steal time from other grants to study DIBs.

### 3. A brief history of DIBs research

The first paper mentioning DIBs, in 1922 (Heger 1922), was published by Mary Lea Heger as a part of her Ph.D. thesis. She was a graduate student at Lick Observatory, now a department of the California university system (first at Berkeley and then at Santa Cruz). Mary Lea was married to Donald Shane, who became director of Lick in 1945; after the marriage her name changed to Mary Lea Heger Shane.

Mary's Ph.D. thesis was on NaI lines, already known to be interstellar because their wavelengths don't change when the two stars in a binary system went through their orbits. She noticed that two broad lines, at 5780Å and 5797Å displayed the same behavior. Apparently she didn't think much of them, only mentioning them in her 1922 paper.

Apparently other astronomers also didn't think much of the broad lines either, because DIBs were not mentioned in research papers in subsequent years, until 1934. Then Paul Merrill, an astronomer at Lick, studied them in detail (1936). He found four more of the lines, and named them the diffuse interstellar bands, and the label stuck. By then, astronomers were aware the DIBs were really interstellar, not circumstellar and not only found in dark clouds.

Arthur Code, in a 1958 paper, suggested that DIBs were discovered much earlier by Annie J. Cannon in her 1890s survey of stellar spectra. Cannon saw a band near 4430Å close to the famous  $\lambda$ 4430 DIB. Later, in 1977, George Herbig examined the same plate that Cannon used and found that that band is stellar, not interstellar (Herbig, private communication). Heger was really the discoverer of DIBs.

In the late 1930s and 1940s, many other prominent astronomers such as Paul Swings (1937; Swings & Rosenfeld 1937); Mefhnand Saha (1937), Otto Struve (1949), Paul Ledoux (1941), Milton Humason (Merrill & Humason 1938), Jesse Greenstein and Aller (1950), Henry Eyster (1937) and Gerhard Herzberg (Douglas & Herzberg 1941), referred to DIBs as caused by simple molecules. Most were diatomic: CN, CH, and CH<sup>+</sup>. Paul Swings and Gerhard Herzberg analyzed this molecular hypothesis, to the point of suggesting the molecular energy levels that could be right for the DIBs. Neither said that they found this was the only source of the DIBs; they only said this could be the mechanism for the DIBs.

Then, in the 1950s to the 1990s, dust grain defects came into the picture. Shapiro argued for dust grains, noting that grain defects could have absorption bands at specific wavelengths, not changing wavelengths or profiles (Shapiro & Holcomb 1986a,b; Shapiro 1995). A few lower-resolution DIB surveys (e.g., Duke 1951; Wilson 1958; Walker 1963; Stoeckly & Dressler 1964; Kristenson & Rudkjobing 1965; Wampler 1966; Deeming & Walker 1967; Gammelgaard 1968, 1975; Kellman 1970) discovered the good correlation between DIBs strength and dust extinction. Dust was in and molecules were out. Note that these correlations were not perfect; they always have some scatter. Possibly of more importance, a straight line through the scatter doesn't go through the origin of the graph, indicating there are DIBs without a significant amount of dust.

In the 1970s three papers made arguments confirming that molecules were involved. The first one (Danks & Lambert 1976) examined the profiles of the 5780Å and the 5797Å DIBs and found that a complex molecule could be the cause. Then, A.E. Douglas (1977), a prominent molecular spectra specialist, argued for long-chain carbon molecules (which

had never been found in diffuse clouds, but he didn't know that). At the same time, a paper (Smith *et al.* 1977) summarized the arguments for molecules, not dust.

The Smith *et al.* paper listed some concerns with the dust hypothesis. Dust grains have inconsistent wavelengths, differing by as much as 100 Å (either to red or the blue), depending on grain size, temperature, and composition. Molecules have none of these inconsistencies. Moreover, dust grains should have polarized profiles but very careful searches for that have come up empty.

By then, using mm-wavelength observations by radio telescopes, OH was discovered (Weinreb *et al.* 1963) followed by many more molecules, growing in complexity. This was consistent with DIBs molecules, but not dust grains. Polycyclic aromatic hydrocarbons (PAHs) are currently favored by many because they are found in the solar system to diffuse to dark clouds (by their IR spectra); they are very stable; and, when ionized, they have a visible spectrum to be compared with DIBs (Leger & D'Hendecourt 1985; Crawford *et al.* 1985; van der Zwet & Allamandola 1985). But no coincidences have found been so far. There are arguments against pure PAHs, but impurities or attached small molecules alter their spectra. A more exotic species that has some resemblance to PAHs, tetrabenzoporphyrin, was proposed by Fred Johnson as the carrier of many DIBs (Johnson 1967, 1972; Johnson *et al.* 1973).

Other suggestions have been published, all containing carbon. The ionized "buckyball" ( $C_{60}^+$ ) was proposed by Foing & Ehrenfreund (1994), with further studies by Galazutdinov *et al.* (2000) and Misawa *et al.* (2009). However, some expected bands are not seen (Maier 1994; Jenniskens *et al.* 1997), and thus the question of DIBs and  $C_{60}^+$  remains unsettled.

John Maier and his group found several coincidences of DIBs with the carbon chain molecule  $C_7^-$  (Tulej *et al.* 1998), but McCall *et al.* (2001), with high-resolution spectra, found that this molecule could not be the source of DIBs because the wavelengths didn't match well enough.

Also the naphthalene cation ( $C_{10}H_8^+$ ) was claimed for one star, Cernis 52 (BD +31 640), because a set of absorption lines matches fairly well the wavelengths of four DIBs (Iglesias-Groth *et al.* 2008). But Searles *et al.* (2011) didn't find those bands in 15 other stars. Cernis 52 was not in this data set though, so Iglesias-Groth could argue that Cernis 52 is special in some way. One star in the Searles *et al.* data set is *o* Per (BD +31 642) which is very close to Cernis 52; both are in the Perseus molecular complex, two arc minutes apart. The question of  $C_{10}H_8^+$  as a source of DIBs remains open.

Krelowski *et al.* (2010) proposed the diacetylene cation  $HC_4H^+$  as the carrier of a DIB at 5069 Å. Further laboratory work by Maier *et al.* (2011a) however then showed that this assignment is very unlikely. Finally (for now) is the proposal by Maier *et al.* (2011b) of  $H_2CCC$  (propadienyldiene) with bands near 4882 and 5450 Å. But again, others (Krelowski *et al.* 2011) have shown that this is not feasible because the DIB strength ratios are not consistent with  $H_2CCC$  and because the inferred column density of  $H_2CCC$  is an order of magnitude higher than CH.

There are ongoing experiments to find the best candidates (Salama *et al.* 2011; Joblin *et al.* 2009; Bierbaum, this volume). It's a difficult problem, because there are very many candidates. Most DIB-candidates were, by far, carbon-bearing molecules. A few do not fit in that category (see Table 1). All of these were unfounded by various astronomers and by various arguments.

#### 4. General characteristics of DIB observations

- (a) DIBs are really interstellar, not circumstellar or in planetary systems (Heger 1922; Merrill 1934).

**Table 1.** Non-carbon DIBs hypotheses:

McKellar, Welsh, & Stephenson (1955)	utracold solid oxygen
Herbig (1963); Malville (1963)	metastable H <sub>2</sub>
Rudkjøbing (1969)	H <sup>-</sup> and O <sup>-</sup>
Manning (1970)	Fe <sup>3+</sup>
Duley (1982)	MgO grains
Duley & Graham (1971)	Ca-C <sub>6</sub> H <sub>6</sub>
Shapiro (1975)	magnetite grains
Duley (1977)	MgO-CaO
Sorokin & Glownia (1996)	H <sub>2</sub> two transition model

- (b) DIBs are best seen against O or B stars, because these stars have relative few intrinsic lines in their spectra, as opposed to cooler stars (Destree *et al.* 2007). But O and B stars usually are fast rotators, broadening their intrinsic lines so much that DIBs can be confused with stellar lines in their spectra. Observing a few other stars, with different spectral types, usually takes care of that.
- (c) Weak DIBs are very difficult to see and analyze, especially with film as the detector. Electronic detectors, such as CCDs, are much better, so film has been phased out. A list of apparent sensitivity helps to see that:

With identical exposure times:

Film:  $\approx 1/20$

CCD  $\approx 1/100$

With longer times:

CCD  $\approx 1/500$  to  $1/1000$  or more (Hobbs *et al.* 2008, 2009).

- (d) DIBs must be formed from common elements. Using HD 183143 as a standard and for common elements (C, O, and N), we get  $N_{\text{DIB}} = 1 \times 10^{15}$  per cm<sup>2</sup>; this is easy to detect. Other common elements (such as Si, Al, Fe, S, etc.) are at least ten times lower than C, N, and O which are also detectable. But for more rare elements (say 100 to 1000 times lower in abundance than O, C and N) there is almost no way to detect them.

Carbon-based molecules are much more likely than other elements for DIBs:

- Its abundance is comparable to oxygen or nitrogen
- It is much more reactive than oxygen or nitrogen
- Silicon, another very reactive element, is ten times less abundant.

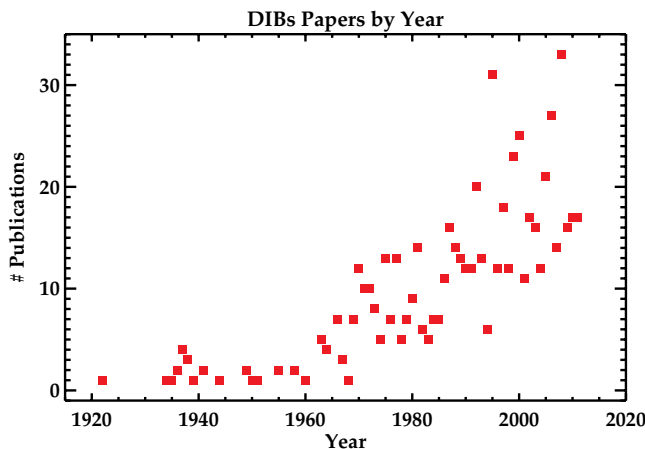
- (e) There are many studies of correlations of DIBs with DIBs and DIBs with extinction and HI and H<sub>2</sub>. No perfect correlations have been found, but at least one is close: the match between the 6196Å and 6613Å DIBs has a correlation coefficient of 0.986 (McCall *et al.* 2010). Paule Sonnentrucker (this volume) has summarized most correlations studies to date.
- (f) DIB strengths and correlations depend on physical conditions, metallicities, and extinction curves (Cami *et al.* 1997; Sonnentrucker *et al.* 1997; Ehrenfreund *et al.* 2002; Welty *et al.* 1997, 1999, 2006; Cox & Spaans 2006; Cox *et al.* 2007b).
- (g) No DIB profiles do show polarization across their profiles (Nandy & Seddon 1970; Martin & Angel 1974, 1975; Fahlman & Walker 1975; Adamson & Whittet 1995; Cox *et al.* 2007a).
- (h) The DIB distribution by wavelength isn't level, but peaks at a particular wavelength, depending on the cloud type (Hobbs *et al.* 2008, 2009; Sonnentrucker, this volume).
- (i) The broad DIBs have no fine structure and have Lorentzian profiles (natural broadening; Snow *et al.* 2002; Snow 2002).

- (j) Narrow DIBs sometimes have asymmetric profiles and/or structure within the profiles, suggesting vibrational levels in molecules (Sarre *et al.* 1995; Kerr *et al.* 1996, 1998; Krelowski & Schmidt 1997; Ehrenfreund & Foing 1996; Cami *et al.* 2004; Galazutdinov *et al.* 2008).
- (k) Searches for circumstellar DIBs have a long history, starting with Snow & Wallerstein (1972) followed 35 years later by Luna *et al.* (2008). The Snow and Wallerstein study was not focused on any specific type of star, but the Luna study was: post-AGB stars. These stars are giants above the main sequence, with fairly dense circumstellar shells.
- (l) DIBs exhibit the so-called edge effect (Wampler 1966; Snow & Cohen 1974; Seab & Snow 1984; Adamson *et al.* 1991), meaning that DIB strengths stop growing with increasing depth in diffuse or translucent clouds. This has to be an environmental effect, and not that they become saturated, because outside of dense clouds the DIBs have a linear growth rate.
- (m) DIBs can be grouped in “families”, having different ratios among DIBs (Krelowski & Walker 1987; Josafatsson & Snow 1987; Kos & Zwitter 2013; Krelowski, this volume). The ratio between the well known 5780Å and 5797Å DIBs is the main criterion to differentiate the two families.
- (n) Normally no DIBs are seen in emission; the Red Rectangle is the only known exception (Sarre 1991; Scarrott *et al.* 1992; Sarre *et al.* 1995; Kerr *et al.* 1996; see also Van Winckel, this volume).
- (o) A few DIBs in infrared wavelengths have been found (Geballe *et al.* 2011; see also Geballe, this volume).
- (p) Searches for ultraviolet DIBs have found almost nothing (Snow *et al.* 1977; Seab & Snow 1985; Clayton *et al.* 2003; Destree & Snow 2009). This may be an ionization effect: ionized DIB carrier molecules are more important in H I regions where UV radiation dominates, but inside H<sub>2</sub> clouds, the DIBs are neutral. This is consistent with Herbig’s (1995) finding that the DIBs are better correlated with H I than with H<sub>2</sub> (see also Friedman *et al.* 2011). Very broad UV DIBs are very difficult to detect and measure because of the complex spectra of O and B stars.
- (q) Extragalactic DIBs are seen in nearby galaxies; e.g. the Magellanic Clouds (Hutchings 1964; Welty *et al.* 1997; Ehrenfreund *et al.* 2002; Welty *et al.* 2006; Cox *et al.* 2007b); M31 and M33 (Cordiner *et al.* 2008a,b, 2011) and QSOs (Heckman & Lehnert 2000; York *et al.* 2006; Lawton *et al.* 2008)

## 5. Constraints on observations of DIBs and laboratory measurements

The following constraints must be taken into consideration when proposing DIB sources:

- (a) The DIBs must be formed of abundant elements.
- (b) Any proposed source must match *all* the bands seen in the lab; not some, but all. On the converse, any observed DIB should be seen in the lab; not one or two. A few identifications in the past had to be discarded by these criteria. These should be obvious but they aren’t, at least by some authors.
- (c) There must be a match between the exact wavelength pattern of the DIB source in the lab spectrum and the interstellar DIBs.
- (d) Similarly, there must be a match between the exact relative strengths in the lab spectrum and the interstellar DIBs.



**Figure 1.** The timeline of DIB papers. This shows that DIB papers have been in publication since 1922, with no significant gaps.

- (e) Different conditions (e.g. temperatures or densities) could change this. We try to emulate the interstellar environment but some experimental conditions are very difficult.
- (f) DIB wavelengths in gas, not solid matrices, must match the observed interstellar wavelengths. Solid matrices always have wavelength shifts.

## 6. Some DIB statistics

Fig. 1 shows the growth rate in the number of published DIB papers, from 1922 until 2011. Almost a century! There is no reason this growth will change in near future. Fig. 2 shows the time distribution of DIB theses since 1971 up to now; another sign of progress. Appendix A lists the people, their Ph.D. year, and their title.

This is said to be the longest-standing unsolved problem in the history of spectroscopy. One would think that with so many people working on the problem, we get to the answer in the end. I think we are making some progress... but we thought that many times.

Remember my warning on the first page: probably there are many different DIBs sources, not just one.

## 7. How to find the papers

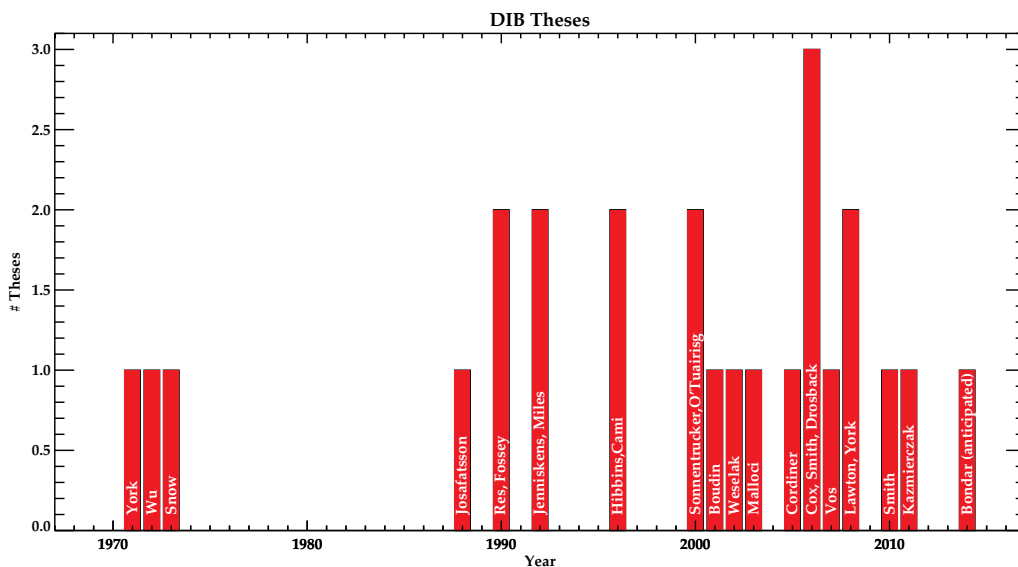
Our group maintains a web site listing all DIBs papers we know of. We update this periodically; we will add any papers we missed. This is the url:

<http://dibdata.org>

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**Figure 2.** DIB theses over time. There are gaps, especially in the past, and growth rising to the present and beyond.

Josh Destree; Jacek Krelowski; Veronica Bierbaum; Valery Le Page; and my graduate students, especially Meredith Drosback, Greg Seab, and Karl Josafatsson; and finally George Herbig. Both the NSF and NASA have given me grants to support my DIBs research.

## Appendix A. DIB Theses

- Don York, 1971: *“Structure in the Interstellar-Extinction Curve”*, University of Chicago, USA.
- Chi-Chao Wu, 1972: *“A Study of the Unidentified Interstellar Diffuse Features”*, University of Wisconsin, USA.
- Theodore P. Snow, 1973: *“The interstellar diffuse bands: a correlation analysis, with comments on suggested Origins”*, University of Washington, USA.
- Karl Josafatsson, 1988: *“Small grains in reflection nebulae: a study of diffuse interstellar bands, elemental depletions and infrared flux”*, University of Colorado, USA.
- Paul Res, 1990: *“The diffuse interstellar features and their interstellar environment”*, NASA Ames Research Center, USA.
- Stephen Fossey, 1990: *“The diffuse interstellar features and interstellar relationships”*, University of London, UK.
- Peter Jenniskens, 1992: *“Organic matter in interstellar extinction”*, University of Leiden, the Netherlands.
- Scarrott, Watkin, Miles, J. R., and Sarre, 1992: *“Evidence for a link between the more prominent optical emission bands in the Red Rectangle and some of the diffuse interstellar absorption bands”*, University of Nottingham, UK.
- Robert Hibbins, 1996: *“Diffuse interstellar bands”*, University of Nottingham, UK.
- Jan Cami, 1996: *Band Correlations and Line Profiles of Diffuse Interstellar Bands (DIBs) in Single-Clouds and DIBs in Reflection Nebulae* (M.Sc. thesis), University of Leiden.



- Paule Sonnentrucker, 2000: “*Large Organic Molecules in Space: Spectroscopic Diagnostics From the Diffuse Interstellar Bands*”, University Louis Pasteur, Strasbourg, France.
- Seathrun O’Tuairisg, 2000: *A deep echelle survey and new analysis of diffuse interstellar bands* (M.Sc. thesis) University of Leiden.
- Nathalie Boudin, 2001: *Recherche de signatures spectrales de cations aromatiques dans l’Absorption Diffuse Interstellaire: Confrontations Spectroscopie de laboratoire - Observations astronomique*, Université Paris-Sud
- Tomasz Weselak, 2002: “*Searching for spectra of Diffuse Interstellar Bands possibly originating at the same carrier*”. N. Copernicus University, Torun, Poland.
- Giuliano Mallocci, 2003: “*Modelling interstellar organics: relevance for the identification of unidentified interstellar features*”, Osservatorio Astronomico di Cagliari, Italy.
- Martin Cordiner, 2005: “*Diffuse interstellar bands and the structure of the ISM*”, University of Nottingham, UK.
- Nick L. J. Cox, 2006: “*Diffuse Interstellar bands and interstellar carbon chemistry in the galaxy and beyond*”, Universiteit van Amsterdam, the Netherlands.
- Arfon Smith, 2006: “*Dust and molecules in interstellar, circumstellar and extragalactic environments*”, University of Nottingham, UK.
- Meredith M. Drosback, 2006: “*Line Profiles in the Diffuse Interstellar Bands*”, University of Colorado, USA.
- Dennis Vos, 2007: “*Diffuse interstellar bands in Upper-Scorpius OB-2 association: Influences of local environmental conditions*” (MSc thesis), Radboud University Nijmegen, Netherlands.
- Brandon Lawton, 2008: “*Diffuse Interstellar Bands in Damped Lyman-alpha and Starburst Galaxies*”, University of New Mexico, USA.
- Brian York, 2008: “*Diffuse Interstellar absorption Bands, Broad Diffuse Band Survey*” (MSc Thesis), University of Vancouver, Canada.
- Keith Smith, 2010: “*Studies of Interstellar Matter on Scales from 10 AU to 10 kpc*”, University of Nottingham, UK.
- Maja Kazmierczak, 2011, “*Centrosymmetric molecules in interstellar clouds*”, Centre for Astronomy, Nicolaus Copernicus University, Poland.
- Arkadii Bondar, 2014: “*High Resolution Survey of DIBs*” (tentative title), Kyiv, Ukraine.

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