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journal homepage: [www.elsevier.com/locate/jms](http://www.elsevier.com/locate/jms)C<sub>60</sub><sup>+</sup> as a diffuse interstellar band carrier; a spectroscopic story in 6 actsH. Linnartz<sup>a,\*</sup>, J. Cami<sup>b,c,d</sup>, M. Cordiner<sup>e,f</sup>, N.L.J. Cox<sup>g</sup>, P. Ehrenfreund<sup>h,i</sup>, B. Foing<sup>j</sup>,  
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## ABSTRACT

In 2019 it was exactly 100 years ago that the first two DIBs, diffuse interstellar bands, were discovered by Mary Lea Heger. Today some 500 + DIBs are known. In numerous observational, modelling and laboratory studies, efforts have been made to identify the carriers of these absorption features that are observed in the light of reddened stars crossing diffuse and translucent clouds. Despite several claims over the years that specific DIBs could be assigned to specific species, not one of these withstood dedicated follow-up studies. An exception is C<sub>60</sub><sup>+</sup>. In 2015, Campbell et al. showed that two strong bands, recorded in the laboratory around 960 nm, coincided precisely with known DIBs and in follow-up studies three more matches between C<sub>60</sub><sup>+</sup> transitions and new observational DIB studies were claimed. Over the last four years the evidence for C<sub>60</sub><sup>+</sup> as the first identified DIB carrier – including new laboratory data and Hubble Space Telescope observations – has been accumulating, but not all open issues have been solved yet. This article summarizes 6 spectroscopic achievements that sequentially contributed to what seems to become the first DIB story with a happy end.

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## Introduction

The number of molecules identified in the interstellar medium has exceeded 200 different species, ranging from simple diatomics to large and complex molecules, both stable and highly reactive [1]. The majority of these species has been found in cold (~15 K) dark clouds and around stars at the end of their lifetime, illustrating a rich chemistry that is driven by reactions both in the gas phase and solid state [2], and that ultimately determine the chemical composition of planetary systems [3–5]. The astronomical identifications generally follow precise radio, sub-mm as well as infrared spectroscopic detections, both in emission and absorption. The number of identified species in diffuse and translucent clouds, however, is restricted to a few tens of species and limited to mainly smaller molecules [1]. The lower column densities in the diffuse

medium limit detection methods mainly to optical absorption spectroscopy. Typically, molecules are identified by looking at absorption features in the light of reddened stars, i.e. stars for which it is clear their light crosses one or more interstellar clouds on its way to Earth. At the same time, along many different lines of sight some 500+ unresolved (that is diffuse) bands have been observed (see for the most recent review [6]), differing in width and intensity, and covering roughly the 400–1000 nm range, with a few bands observed in the near infrared. These bands are known as the diffuse interstellar bands, DIBs [7–10]. Given their strength, it is clear that DIBs must originate from abundant molecular species, but unambiguous identifications have not been possible, despite substantial progress both in laboratory and observational studies. Over the years, evidence has been accumulating that DIBs are related to electronic transitions of carbonaceous gas phase material. Many different carriers have been proposed and tested in the past, varying from carbon chain radicals [11] to polycyclic aromatic hydrocarbon cations [12], and generally resulting in neg-

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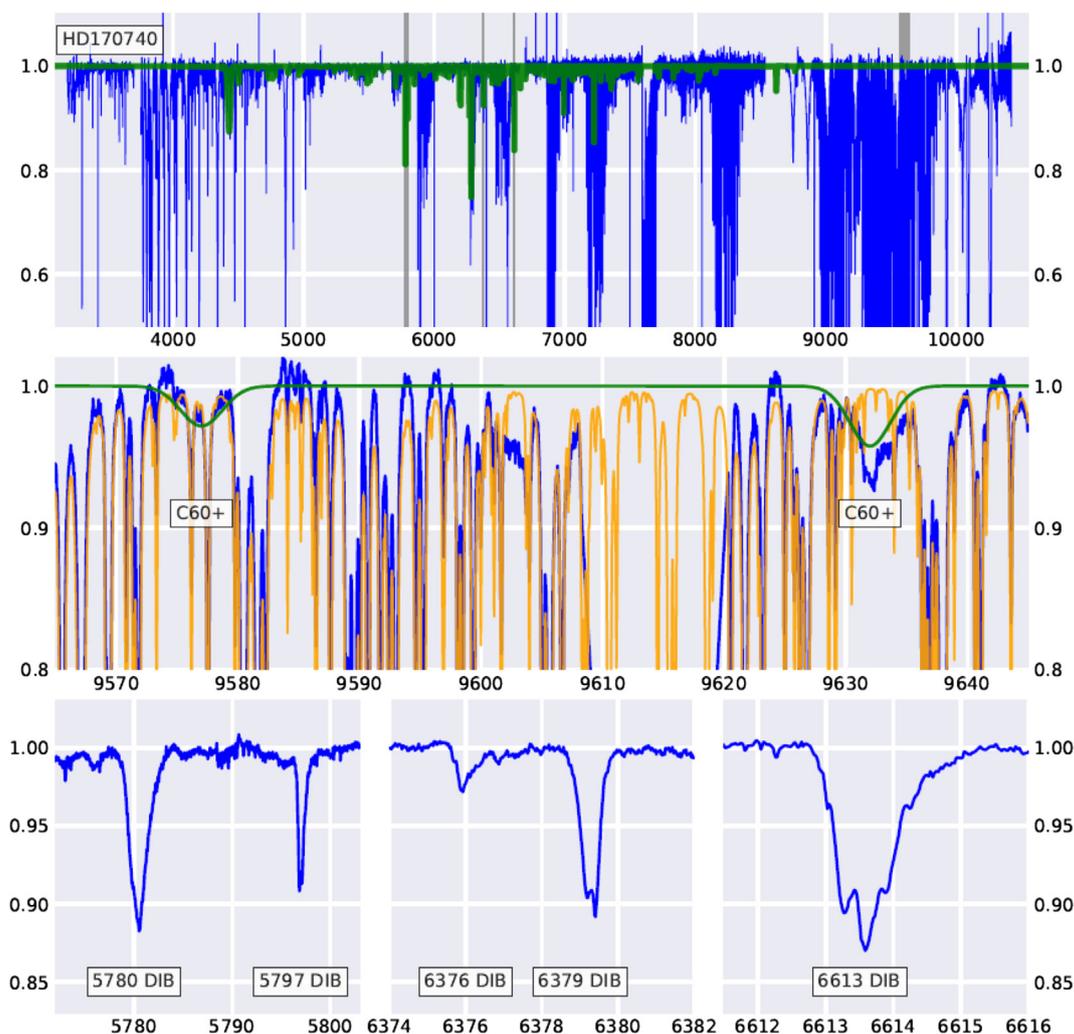
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ative results. Reported overlaps, like for  $C_7^-$  [13],  $HC_4H^+$  [14] and  $I-C_3H_2$  [15] turned out to be coincidental and were shown not to be real matches. A remarkable exception, however, is the fullerene cation  $C_{60}^+$ , and the result of 25 years of dedicated spectroscopic work, both in the laboratory and behind the telescope. Below follows a spectroscopic story in six acts.

#### Act 1: DIBs surveys

In 1919 Mary Lea Heger, studying the interstellar Sodium lines towards spectroscopic binaries, observed two broad features around 5797 and 5780 Å, that were reported in the literature a few years later [16]. It was clear that these bands found their origin in interstellar gas and dust [17] but the exact nature of the bands remained unclear. Today, a century later, a substantial number of DIBs has been reported, among others following dedicated astronomical surveys. See e.g. Refs. [18–21] and for an overview of more recent surveys Refs. [6,22], resulting in some 500+ DIBs, mainly in the UV–VIS, and extending into the NIR. These bands differ substantially in linewidth and intensity. The majority of these studies focused on the properties of a small number of DIBs, for selected wavelength ranges and for specific astrophysical environments, whereas more recently also high-quality surveys of interstellar fea-

tures over large spectral ranges and towards different interstellar environments have become available [6,22]. All these surveys exhibit features that are due to known interstellar atoms and small molecules (e.g., CN,  $C_2$  or  $OH^+$ ) and that can be used as diagnostic tools to accurately define the physical conditions in the environments DIB carriers reside.  $OH^+$ , for example, offers a tool to determine the value for the cosmic ray ionization rate [23] and  $C_2$  abundances are found to correlate with a selected number of DIBs [24]. The upper panel of Fig. 1 shows a typical ground-based overview spectrum, taken from one of the many lines-of-sight investigated within the framework of EDIBLES, the ESO Diffuse Interstellar Band Large Exploration Survey (EDIBLES) [22]. EDIBLES is a large observing program at the UVES spectrometer at the Very Large (8.2 m) Telescope at Paranal and quite unique in its combination of spectral resolution, wavelength coverage, sensitivity and sample size. Also shown in this panel is a synthetic DIB spectrum. The middle panel shows that despite reasonable to good atmospheric conditions, many telluric contaminants show up that must be considered properly. This is a general issue inherent to ground based observations, particularly towards the near-infrared spectral range where the  $C_{60}^+$  bands are located. The bottom panel shows a selection of several DIBs, partially also showing substructure that has been linked to unresolved rotational contours.



**Fig. 1.** The upper panel shows a complete EDIBLES spectrum towards HD170740 (blue). This spectrum is one representative spectrum of more than 100 similar spectra recorded along different lines-of-sight. Also a synthetic DIB spectrum is shown, based on measurements towards HD183143 (green, from Hobbs et al. 2009). The middle panel shows a zoom-in of the  $C_{60}^+$  region. The blue line shows the EDIBLES spectrum, the orange shows the heavy telluric pollution in this wavelength region. The bottom panel shows zoom-ins of a number of well-known DIBs; the 5780 + 5797, 6376 + 6379 and 6613 DIBs, partially showing substructure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

What can be learned from such surveys? The high spectral resolution allows us to determine accurate peak positions and band profiles (intensity, FWHM, detailed line shapes) that can be directly compared to spectra simulated for different conditions, e.g. rotational temperatures, based on accurate constants as derived from laboratory studies. The latter are performed under fully controlled conditions and can be linked to specific molecules. Some DIBs are exceptionally broad and exhibit a clear Lorentzian band profile that is likely the result of lifetime broadening – this is then also visible in the laboratory [25] – other DIBs show some substructure that may be caused by unresolved rotational contours rather than partially overlapping features from different DIBs. Here fully resolved laboratory data allow to simulate absorption profiles for different temperatures (see e.g. [11]). In fact, bands with substructures, as shown in the lower panel of Fig. 1, offer a tool for size estimates for their carrier molecules [26,27]. The high sensitivity facilitates studying both strong and weak DIBs simultaneously. This is relevant as it is likely that any given DIB carrier is not just represented by one band only, but in addition exhibit (weaker) vibrational progressions. In the past, it has been put as an explicit prerequisite for a DIB match that not only the origin band, but also (weaker) transitions involving the vibrational signature of the excited electronic state show up in the astronomical data. It was for this reason that the C<sub>7</sub> case looked so convincing, as initially (near) overlaps with 8 separate bands were found [13]. Moreover, high-resolution, high-S/N spectra hold the potential to show subtle profile variations for different lines of sight (i.e., for different environmental conditions, such as the intensity of radiation fields) or even with time towards one specific target, i.e., when the proper motion of a background star results in lines-of-sight monitoring different areas of an intervening cloud.

A good characterization of all these features aids the search for the most likely DIB carrier molecules.

#### Act 2: Matrix data

DIB carriers can only be assigned after comparison of astronomical data with spectra accurately characterized in the laboratory. In the late 80s and 90s of last century it was suggested that DIBs do not originate from stable or easy to form molecules, i.e., species for which gas phase spectra were generally available. Instead the laboratory research focused on transient species, such as molecular radicals and ions that are likely to be present in regions in space where chemistry is largely dominated by intense radiation fields. However, with the available technology such species were hard to generate with sufficiently high abundances in the gas phase and here matrix isolation spectroscopy offered a powerful alternative [28–31]. In a matrix setup, ions can be deposited, over hours, mass selectively, in a cryogenic (~4–30 K) and generally chemically inert environment, yielding ion densities of, up to 10<sup>15</sup>–10<sup>16</sup> particles/cm<sup>3</sup>. For such high densities even a rather insensitive method as Fourier transform direct absorption spectroscopy turns out to provide excellent spectra. Over the years this has yielded hundreds of spectra of hydrocarbon radicals recorded in different types of rare gas matrices, not only of cations, but also of their neutral and anionic equivalents, applying annealing techniques. Unfortunately, all these spectra come with shifts that are caused by matrix interactions; even in the case that the interaction is weak, shifts can amount to as much as several tens of cm<sup>-1</sup>, typically up to as much as a few tens of line widths, and therefore far beyond the accuracy needed to compare laboratory and astronomical data. To date the absolute observational and laboratory accuracies in the VIS-NIR domain are of the order of 0.1–0.5 cm<sup>-1</sup>. Nevertheless, in 1994 Foing and Ehrenfreund linked two strong absorption bands at 9580 ± 4 and 9642 ± 3 Å, recorded for C<sub>60</sub><sup>+</sup> embedded in rare

gas matrices [32] to possible DIBs. Extrapolating the laboratory matrix data to possible gas phase values, they detected these two new near infrared DIBs, using a 1.5 m Coudé telescope [33]. The involved shifts between matrix laboratory and astronomical gas phase data of the order of several tens of cm<sup>-1</sup> made sense; for the lowest electronic transitions of neutral C<sub>60</sub> around 6300 Å, a shift of 50 cm<sup>-1</sup> was reported between neon matrix and gas phase spectra [34]. Smaller shifts are expected for infrared transitions involving deeper states [35], which concurs with a shift of only 10 cm<sup>-1</sup> between the astronomical and neon laboratory C<sub>60</sub><sup>+</sup> data [36]. The two C<sub>60</sub><sup>+</sup> bands showed the same separation (61 ± 10 and 62 ± 6 Å) in Ar and Ne matrices [32] and at that time were attributed to two major ground state geometries favored by Jahn-Teller types of distortion [37]. The two states would be populated depending upon excitation, leading to variations in the measured line ratios peaks in the neon matrix data. Following the findings presented in Ref. [33], several groups tried – without success – to record the corresponding C<sub>60</sub><sup>+</sup> gas phase spectra.

#### Act 3: Tagging methods and gas phase data

The recording of accurate spectra of C<sub>60</sub><sup>+</sup> in the gas phase is hard. This requires C<sub>60</sub> powder to be brought into the gas phase, ionized and with densities high enough to be observable by spectroscopic techniques. Direct absorption spectroscopy is a method that is generally applicable and ideal to compare with DIB spectra, but it comes with relatively low detection sensitivity, even when sophisticated modulation [38], cavity enhanced (e.g. cavity ring down spectroscopy – CRDS [39,40]) or REMPI techniques [41] are applied. Over the years the latter and other methods have been used to record precise spectra in adiabatically cooled plasma expansions, resulting in high resolution electronic spectra for a large number of pure and hydro-carbon radicals, all considered to be possible DIB carriers. From this work, many species could be excluded as possible DIB carriers, and in the case of other species, spectral overlaps were shown to be coincidental. This latter is not too surprising, given the large number of known DIBs; in the red part of the electromagnetic spectrum, for example, on average, there is one DIB per Angstrom, i.e. the chance on a coincidental overlap is high. Special care is needed, therefore, to distinguish between an overlap and a match. Attempts to use the methods mentioned above to record C<sub>60</sub><sup>+</sup> gas phase spectra failed.

A good, but experimentally challenging alternative to these methods is to use tagging-methods combined with mass spectrometric detection. The basic concept is that a molecule is tagged to another species, typically through a weak (i.e., van der Waals-like) bond. Upon molecular excitation, energy redistribution causes the complex to dissociate and this can be monitored by recording either the decrease in mass signal for the complexed species or the increase in mass signal for the resulting ion fragments. As this process is wavelength dependent, spectra can be recorded by monitoring the changing mass signal upon laser tuning. Tagging techniques are well known and have been used for example to study many ionic complexes [42]. As this method is essentially background free, precise spectra can be recorded for very low molecular abundances. A disadvantage of molecular tagging, however, is that even a weak bond will change the energy levels of the original molecule, like in a matrix environment, and consequently, tagging spectroscopy in first instance addresses the properties of the complexed molecule and not those of the non-complexed species.

In 2015, Campbell et al. [43] recorded the spectra of C<sub>60</sub><sup>+</sup>-He<sub>n</sub>, with n varying from 1 to 4, using ion trap technology. Such traps have the advantage that much lower molecular abundances are needed (some 10<sup>4</sup> ions/cm<sup>3</sup> vs. 10<sup>8</sup>–10<sup>10</sup> ions/cm<sup>3</sup> in CRDS studies)

to obtain a detectable signal. Using a 22-pole ion trap [44] as pioneered by Gerlich and co-workers [45], they found that the wavelengths shifted linearly with the number of attached He-atoms, approximately  $0.2 \text{ \AA}/\text{He-atom}$ , from which the un-complexed ( $n=0$ ) rest wavelengths could be derived. Given the high symmetry of  $\text{C}_{60}^+$  this method works, even though there exist in principle two different surface areas (a pentagon or hexagon ring) above which a He-atom can be situated. In fact, spectra for the two  $\text{C}_{60}^+$ -He isomers were also separately recorded in a later study [46], but for larger  $n$ -values the small differences in energy averages out. In this way the tagged ion trap spectra provided extrapolated gas phase wavelengths for five  $\text{C}_{60}^+$  bands, at 9632.7, 9577.5, 9428.5, 9365.9, and 9349.1  $\text{\AA}$  [43,47], with a precision of the order of 0.1  $\text{\AA}$ , high enough to directly compare with or to guide astronomical observations. Moreover, for the tagged species band profiles and intensity ratios could be determined, parameters that are also of high relevance to add further proof or to disprove that laboratory data match DIB features.

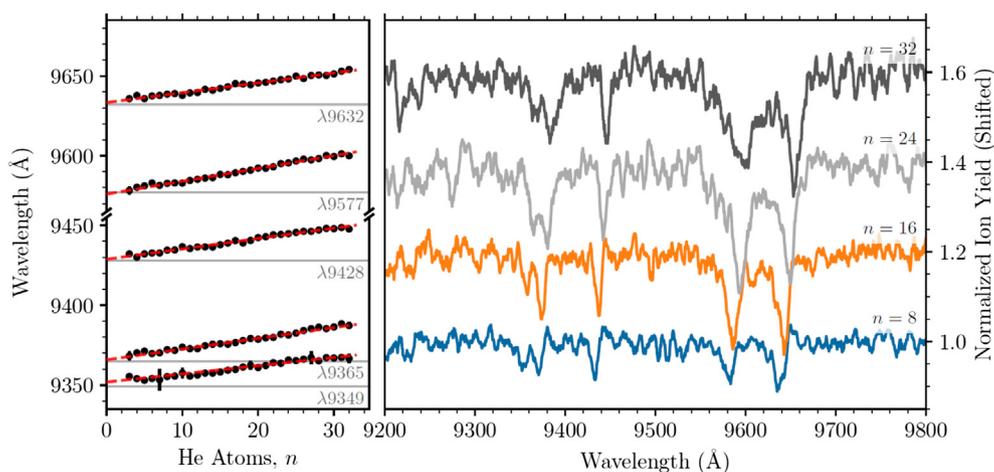
In the same period, data became available from  $\text{C}_{60}^+$  embedded in He-droplets, recorded by Kuhn et al. [48], initially with the aim to investigate the He solvation behavior of fullerene ions embedded in these ultra-cold environments. The basic principle of this method – ionizing doped He-droplets, typically comprising 10-thousands of He-atoms – is different from the ion-trap approach, but it also can be considered a tagging method. Depending on the conditions used, the number of He atoms in a droplet can be varied. Upon electron impact ionization, the embedded ions may be ejected from the droplets, often solvated in smaller quantities of He, leaving  $\text{C}_{60}^+$ -He $_n$  clusters with a large range in  $n$ -values, from  $n=1$  to several hundreds. Spectra are subsequently obtained by recording the mass loss for the selected  $\text{C}_{60}^+$ -He $_n$  species upon resonant laser excitation using a time-of-flight spectrometer. The main difference with the earlier mentioned ion trap tagging is that in the case of  $\text{C}_{60}^+$  embedded in He droplets, much larger  $\text{C}_{60}^+$ -He $_n$  complexes can be studied. Also, the initial temperatures are lower ( $\sim 0.4 \text{ K}$  vs.  $\sim 5 \text{ K}$ ). Particularly the first 32 He-atoms attached to  $\text{C}_{60}^+$  are important, as in this range peak positions still shift linearly with increasing  $n$ -value, allowing to confirm the rest wavelengths derived in the ion-trap experiment. The physical chemical principle is the same as in the ion trap experiment; each He-atom has about the same distance to the  $\text{C}_{60}^+$  core and is determined by a

binding energy of  $\sim 9 \text{ meV}$  and contributes a similar amount to the red shift of the absorption wavelength with respect to the bare chromophore. This is illustrated in Fig. 2.

In the right panel the  $\text{C}_{60}^+$  bands are shown for  $\text{C}_{60}^+$ -He $_n$  with  $n=8, 16, 24$  and  $32$ . The band positions clearly shift. In the left panel this shift is shown for all five  $\text{C}_{60}^+$  bands for all  $n$ -values up to  $n=32$ . The first 32 He-atoms fill up the available space above the 12 pentagons and 20 hexagons, barely interacting with each other. Once these spaces are taken, the process loses its linear dependency as the first layer of He atoms is partially displaced [48]. Using this He-droplet method the band origins for five non-complexed  $\text{C}_{60}^+$  bands were derived, using an extrapolation based on 32 instead of 4 data points (left panel Fig. 2). The resulting values were very close to the values found in the ion trap experiment. Again, the extrapolation method works well, because of the high molecular symmetry of  $\text{C}_{60}^+$ . Using the same method for molecules with a much lower geometry, like PAH cations, clearly shows that for a correct interpretation of the tagging process, accurate structural information on the tagged molecule is needed [49].

#### Act 4: Fullerenes in space

The 90s were the golden years for fullerene research. The discovery of  $\text{C}_{60}$  and  $\text{C}_{70}$  in the laboratory in 1985 [50], resulted in a Nobel Prize for Smalley, Kroto, and Curl. Fullerenes were found to exist and form in many different environments, in fact, they turned out to be quite common products in combustion processes, but their presence in space, generally expected [51], could not be proven for a long time. Indeed, as soon as spectroscopic data on  $\text{C}_{60}$  was available, astronomers started observing. Dedicated searches for the electronic transitions of  $\text{C}_{60}$  in the optical turned out negative [52–54]. Searches for the IR vibrational signatures of  $\text{C}_{60}$  using the Infrared Space Observatory (ISO) did not fare any better [55,56]. It took the much better sensitivity of the Spitzer Space Telescope to finally find these elusive species. Sellgren et al. [57] presented a very detailed study of high-resolution spectra in the 15–20  $\mu\text{m}$  region with Spitzer's Infrared Spectrograph (IRS) of the reflection nebula NGC 7023. They noticed emission features at 17.4 and 18.9  $\mu\text{m}$  and discussed in detail that these could well be due to  $\text{C}_{60}$ . Contamination by PAH bands caused some confusion, and because they had no access to the shorter wavelengths



**Fig. 2.** The two panels illustrate how to compare the  $\text{C}_{60}^+$ -He $_n$  droplet laboratory data with astronomical spectra. The right panel shows for four selected  $n$ -values (8, 16, 24 and 32) the  $\text{C}_{60}^+$  transitions around 9633, 9578, 9428, 9365 and 9349  $\text{\AA}$ . The band positions shift with  $n$ , because of the tagging effect. The shift is linear for  $n$ -values up to 32, because of the high molecular symmetry of  $\text{C}_{60}^+$ . This effect is shown for the five transitions for all  $n$ -values from  $n=3$  to  $n=32$  in the left panel. As discussed in Ref. [48] this allows to derive the un-tagged free ( $n=0$ ) gas phase value for each  $\text{C}_{60}^+$  transition through extrapolation. These values fully overlap with the astronomical HST data as presented in Fig. 3.

at that time, they could not detect the other two bands at 7.0 and 8.5  $\mu\text{m}$  for confirmation. In the treasure trove of Spitzer observations, Cami et al. [58] found the entire spectrum of the planetary nebula Tc 1. These observations convincingly showed the presence of not only all vibrational modes of  $\text{C}_{60}$  but also those of  $\text{C}_{70}$  in one and the same spectrum, and this without contamination by PAH bands. At about the same time, Sellgren et al. [59] confirmed the 7.0  $\mu\text{m}$  and 8.5  $\mu\text{m}$  bands in NGC 7023. Since then,  $\text{C}_{60}$  has been found in a large number of quite diverse astrophysical environments: in many planetary nebulae (see e.g. [60–63]) and other evolved stars [64–67], but also in reflection nebulae [59,68,69], young stellar objects [70] and the diffuse interstellar medium [71], in line with the idea that  $\text{C}_{60}^+$  can originate from its neutral precursor upon vacuum UV irradiation. Fullerenes are thus indeed widespread and abundant in space – as Kroto had predicted in 1985.

#### Act 5: Ground based and Hubble Space Telescope observations

With the availability of accurate  $\text{C}_{60}^+$  laboratory gas phase data it became possible to compare these spectra with astronomical data. For the two stronger DIBs, at 9633 and 9578 Å, accurate observations were already available [33], and the comparison between laboratory results and astronomical spectra showed convincing overlaps, both in wavelength and approximate bandwidth. Following the laboratory data, new observational attempts were made to identify also the other three weaker  $\text{C}_{60}^+$  bands. These attempts were complicated by severe telluric pollution; in the range of the  $\text{C}_{60}^+$  bands a series of strong water absorptions is situated. Nevertheless, Walker et al. [72,73] presented the detection of the three weaker bands, at 9428.5, 9365.9, and 9362.5 Å. These bands were not observed simultaneously, along one line of sight, but merely complementary towards different targets. This raised a debate, also given the generally lower signal-to-noise ratios, whether the claimed detections were real or (partly) a result from the data processing [74–77]. It was found that the 9428 DIB was non-detectable in follow-up studies, even when the same data sample was used. This conflicted with the initial laboratory results by Campbell et al., who showed that this specific DIB should be about 1.5 times stronger than the 9365 band that could be identified in the astronomical control surveys. Moreover, the intensity ratio of the two strongest  $\text{C}_{60}^+$  DIBs became topic of discussion. In 2000, it was concluded that this ratio is constant within 20% uncertainty [78], consistent with the assumption that both bands originate from the same carrier. In more recent work, Galazutdinov and

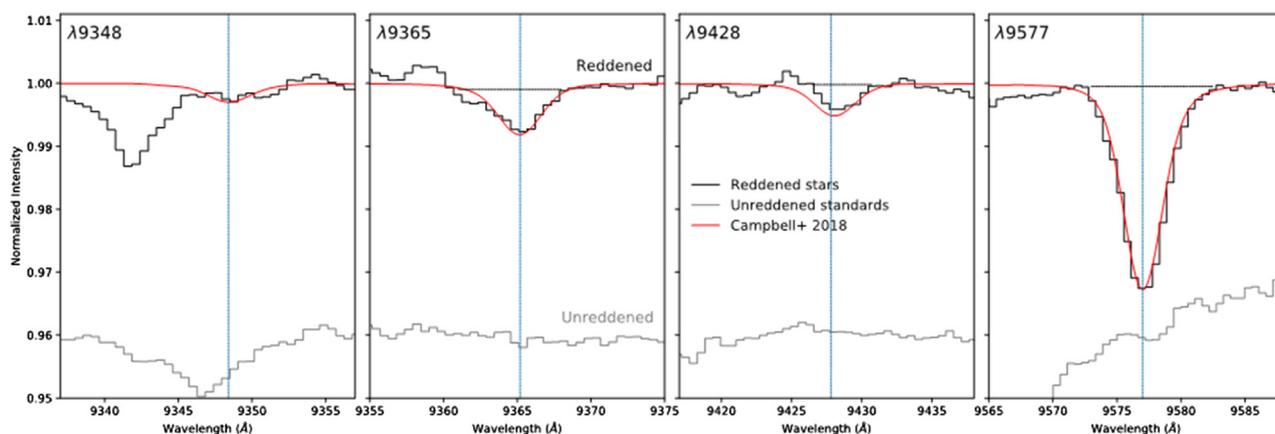
co-workers [75], presented a different conclusion for a substantial number of lines-of-sight with rather strongly varying 9633/9578 intensity ratios. When both bands originate from transitions starting from the same level in the  $^2\text{A}_u$  ground state, such a varying value is not *a priori* expected.

Up to recently, it was unclear whether these inconsistencies are caused by error-prone telluric-correction methods or find their origin elsewhere. A way to circumvent atmospheric issues is by recording telluric free spectra. This is only possible using the Hubble Space Telescope (HST). Cordiner et al. [79,80] used a new method for ultra-high signal-to-noise ratio (S/N) spectroscopy of background stars in the near-infrared (0.9–1  $\mu\text{m}$ ), using the HST Imaging Spectrograph (STIS) in a previously untested “STIS scan” mode.

A zoomed-in view of the spectral regions surrounding four of the five interstellar  $\text{C}_{60}^+$  features is shown in Fig. 3. This was obtained by taking the average spectra from five heavily-reddened sightlines, so as to reduce the statistical noise, average out continuum uncertainties, and reduce the impact of individual stellar features (due to their differing Doppler shifts between stars). Prior to averaging, the individual (reddened) target spectra were shifted to the interstellar rest frame, based on high-resolution KI observations. A (Doppler broadened) comparison laboratory spectrum from [46] has been overlaid in Fig. 3.

The astronomical spectra for the 9578, 9428 and 9365 bands are convincing and in the case of the weakest (9349) band hint for a coincidence. The HST grating settings did not allow to study also the 9633 band in one run. Either the two most red, i.e. the two strongest DIBs or the four most blue, i.e. the three weaker DIBs plus the 9578 DIB could be monitored simultaneously. As the goal was to search for the weaker DIBs, the latter setting has been used. The intensity ratios between the three (four) observed bands and the ion trap and helium droplet laboratory data agree well. Also, the linewidths (FWHMs of the order of 2–2.5 Å) are very similar in the observational and laboratory spectra, particularly when taking into account that the latter values only can be derived for the  $\text{C}_{60}^+$  complexed molecules.

In the initial HST [79], the 9578 DIB could be easily recorded, but a suboptimal target choice prohibited an unambiguous identification of the three weaker bands; the selected line of sight was known to be rich in DIBs, but UV (ionizing) radiation fields turned out to be low, likely reducing  $\text{C}_{60}^+$  abundances below an unambiguous detection limit for the weaker bands. In the follow-up study [80], more HST orbits were allocated and different targets could be studied. This study resulted in clear identifications of the 9578, 9428



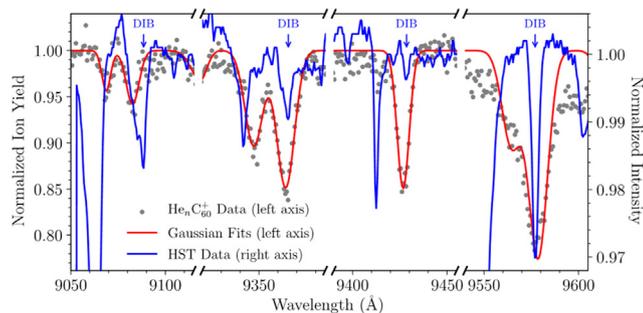
**Fig. 3.** Mean HST STIS spectra observed towards 5 heavily-reddened early B-type stars, in the interstellar KI rest frame (corresponding mean spectra for the un-reddened standard stars are shown in grey). Laboratory comparison spectra taken from [46] are shown in red. These are convolved with a Gaussian broadening kernel of FWHM = 80 km/s.

and 9365 bands. The spectra showed that the 9428 DIB is weaker than the 9365 DIB, a finding in agreement with more recent laboratory data on  $C_{60}^+$  [46] in which the 9428 band was presented to be about 1.5 times weaker than the 9365 band. Therefore, based on the numbers available at that time, the initial criticism in Ref. [75] was not fully misplaced. In the HST study, no proof was found for a band around 9349 Å; as this band is even weaker than the 9428 Å band, it may be wise to recheck the corresponding identification using ground based data presented in Ref. [73].

As said, the used HST grating settings did not allow to record the two stronger DIBs simultaneously. For this reason, it has not been possible, yet, to compare the 9633/9578 intensity ratios of these two DIBs along different lines of sight. Such work will take out atmospheric uncertainties in the band intensities, but even then, it is likely that this is still not sufficient to fully address the variable 9633/9578 intensity ratios; the 9633 DIB overlaps with a MgII stellar line. For hot massive stars, the typical targets in DIB surveys, the modelling of such an atomic line is far from trivial. An alternative approach may be through a target selection for which the Mg II line is shifted away from the DIB feature, or to focus on intensity ratios of the other (MgII free)  $C_{60}^+$  DIBs. This will need future action.

The HST work [79,80] also resulted in the confirmation of previously claimed new DIBs at 9088 and 9412 Å [78], in a region where more (and generally weaker)  $C_{60}^+$  bands were found [47,81]. It is a logical next step to investigate whether these bands are connected to  $C_{60}^+$  transitions as well. For this it is important to understand the molecular origin of the observed transitions. In Ref. [82] several (past) assignments were discussed and using electronic structure methods the 9365 and 9578 bands were (re)assigned to a  ${}^2A_u(v=0) \rightarrow {}^2A_g$  electronic transition, with  $v'=0$  for the 9578 band and  $v'=1$  for the 9365 band. In a similar way, the 9428 and 9633 bands were assigned to the  ${}^2A_u(v=0) \rightarrow {}^2B_g$  transition with  $v'=0$  and 1, respectively. Here the  ${}^2A_g$  and  ${}^2B_g$  states represent the lowest  ${}^2E_{1g}$  state that is split by Jahn-Teller distortion. In this theoretical study, rovibrational coupling is thought to affect the Franck-Condon factors and therefore band intensities, possibly affecting the intensity ratios of the two strongest DIBs for different rotational distributions because of environmental differences in the ISM.

Fig. 4 shows a comparison between the HST data and recently obtained He-droplet data. Here the  $C_{60}^+$  spectrum is generated by stacking the  $C_{60}^+$ -He $_n$  data from a range of  $n$ -values ( $n \leq 32$ ) and simultaneously correcting for the shifts of the individual  $n$ -



**Fig. 4.** Comparison of  $He_n C_{60}^+$  photofragmentation spectra in the He droplet experiments with the spectrum obtained with the HST. The  $He_n C_{60}^+$  spectrum is produced by correcting and stacking the data from a range of  $n$ -values ( $n \leq 32$ ), improving S/N ratios and also broadening features. The small shoulder to the left of the 9578 Å band is a result of different interaction strengths between the He atoms and the pentagonal and hexagonal faces of the  $C_{60}^+$  ion. Besides the  $C_{60}^+$  bands discussed here, two new features can be seen that are close to (but not fully overlapping with) DIBs reported recently around 9088 and 9412 Å. New  $C_{60}^+$  laboratory data have been found below 9050 Å as well, not shown here.

values. This results in substantially improved S/N ratios. Intensity ratios, however, cannot be directly compared. The figure shows that the two newly confirmed DIBs, mentioned above, are close (but not fully overlapping) with two clear  $C_{60}^+$  bands and currently work is in progress to further characterize these two and several other new  $C_{60}^+$  laboratory bands, in order to link these correctly with the astronomical data. These bands are in a wavelength region where one would expect transitions in the  $v'=2$  upper electronic state; an identification of the vibrational progression of doublets, therefore could add further spectroscopic proof to the identification of  $C_{60}^+$  as a DIB carrier. The stacking also leads to a broadening of the bands. This is in part due to different interaction strengths between the He atoms and the pentagonal and hexagonal faces of the  $C_{60}^+$  ion, as discussed earlier in Ref. [46]. For the 9578 Å band this is visible as the small shoulder on the blue side of the laboratory spectrum.

#### Act 6: Astrochemical modeling

$C_{60}$  exists in space and upon UV irradiation the fullerenes ionize. Upon electron recombination, they may also become neutral again, but the fact that the  $C_{60}^+$  signals in Ref. [79] were substantially weaker compared to the results in Ref. [80], i.e., recorded in environments that are more radiation dominated, the charge balance may be on the positive side.  $C_{70}$  also has been discovered in space, and in a similar way  $C_{70}^+$  is expected to be present, but substantially higher column densities are needed to obtain signal strengths comparable to that of  $C_{60}^+$ ; the  $C_{70}^+$  oscillator strengths are substantially smaller [47].

The main question is: why is  $C_{60}^+$  present in the diffuse interstellar medium at all? The largest pure carbon species, identified before, was  $C_3$  [83,84]. Spectra were recorded, fully rotationally resolved, for both the origin band and several transitions involving vibrationally excited states in the upper electronic state [84], but astronomical searches for  $C_4$  and  $C_5$  were unsuccessful. So, is there an astrochemical model that can explain the carbon gap between  $C_3$  and  $C_{60}$ ?

The idea has been proposed that fullerenes may form in a top-down scenario, i.e., along a pathway in which larger molecules (with more than 60 C-atoms) transfer into fullerenes. This applies to very large polycyclic aromatic hydrocarbons. The presence of PAHs in space is generally accepted and linked to the UIRs, the unidentified IR emission bands that have been assigned to vibrational relaxation from UV excited PAHs [85]. PAHs were shown to effectively ionize upon UV irradiation [86] and to fragment. In a laboratory study investigating the photo-fragmentation behavior of  $C_{66}H_{48}$  it was found that at least a substantial part can transfer into  $C_{60}^+$  [87]. The precursor species first loses its H-atoms, subsequently the further loss of a  $C_2$ - or  $C_2H$ -unit starts bowling the PAH plane, slowly curving it into a fullerene (alike) molecule. This concept was earlier introduced on the basis of astrochemical modeling to explain interstellar  $C_{60}$  [88,89] and meanwhile also several other interstellar bowling and curving mechanisms have been proposed [see e.g. 90]; the presence of fullerenes in space may be the direct consequence of molecular processes bowling graphene planes. If correct, this also means that the chemical inventory of the diffuse medium is much more complex than assumed so far. In fact, one could argue that many of the 500+ still unassigned DIBs are due to PAH-derivatives. In the past, different and mainly commercially available PAHs (and their cations) have been studied in the laboratory and none of the recorded spectra showed a convincing overlap with known DIB features (see [91] and references therein). Possibly only larger PAHs are able to withstand the strong interstellar radiation field and this may open new ideas for other DIB carriers; protonated and dehydrogenated PAHs or larger (rad-

ical) PAH fragments, charged or neutral. The experiments in Ref. [92] on HBC (*hexa-peri-hexabenzocoronene*) cations showed that upon photo-induced fragmentation, particularly  $C_{32}^+$  is interesting; this seems to form a molecular sinkhole in the dissociation process and therefore could be much more abundant in space than expected. Attempts to isolate this ion and measure its optical (gas phase) spectrum were not successful yet. It is also possible that the decreasing ionization potential with increasing charge state, would allow the presence of multiple charged species, PAHs and fullerenes, in translucent clouds. All these potential DIB carriers have been topic of spectroscopic discussions [93], but accurate laboratory spectra to compare such species with DIB features are largely lacking, generally because of experimental limitations. Even sensitive tagging methods may not be as efficient as for  $C_{60}^+$ , as most species have a much lower symmetry, causing tags to connect to different molecular sites which results in different spectral shifts, and consequently much harder to derive wavelengths for the un-tagged species [49].

Another possibility is that fullerenes are so stable that they simply survive their formation after the stellar AGB phase, for millions of years; e.g. fullerenes would be cold molecular witnesses of the carbon rich end of a dying star and then may be linked to other DIBs, following chemical processes starting from this point, i.e. protonation ( $HC_{60}^+$ ), ongoing ionization ( $C_{60}^{2+}$ ,  $C_{60}^{3+}$ ), see e.g. [86], or perhaps even fullerene or PAH-fullerene complexation.

It is clear, the number of possible DIB candidates remains as impressive as ever before, but the strong proof for  $C_{60}^+$  as a DIB carrier makes that earlier speculations towards larger and more complex species now have a valid base. Moreover, correlations between the  $C_{60}^+$  DIBs and other DIBs may hint for a shared chemical history. After 100 years, DIBs still form an intriguing research topic, and a small tip of the veil has been lifted now. The story continues.

### CRedit authorship contribution statement

**H. Linnartz:** Writing - original draft, Writing - review & editing, Investigation and Methodology. **J. Cami:** Investigation and Methodology. **M. Cordiner:** Investigation and Methodology. **N.L.J. Cox:** . **P. Ehrenfreund:** Investigation and Methodology. **B. Foing:** Investigation and Methodology. **M. Gatchell:** Investigation and Methodology. **P. Scheier:** Investigation and Methodology.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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