Fullerenes in space

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Abstract

In 1985 the football structure of C_{60}, buckminsterfullerene was proposed and subsequently confirmed following its macroscopic synthesis in 1990. From the very beginning the role of C_{60} and C_{60}^+ in space was considered, particularly in the context of the enigmatic diffuse interstellar bands. These are absorption features found in the spectra of reddened star light. The first astronomical observations were made around one hundred years ago and despite significant efforts none of the interstellar molecules responsible have been identified.

The absorption spectrum of C_{60}^+ was measured in a $5\,K$ neon matrix in 1993 and two prominent bands near $9583\,Å$ and $9645\,Å$ were observed. On the basis of this data the likely wavelength range in which the gas phase C_{60}^+ absorptions should lie was predicted. In 1994 two diffuse interstellar bands were found in this spectral region and proposed to be due to C_{60}^+. It took over 20 years to measure the absorption spectrum of C_{60}^+ under conditions similar to those prevailing in diffuse clouds. In 2015, sophisticated laboratory experiments led to the confirmation that these two interstellar bands are indeed caused by C_{60}^+, providing the first answer to this century old puzzle. Here, we describe the experiments, concepts and astronomical observations that led to the detection of C_{60}^+ in interstellar space.

1 Discovery of the fullerenes

In 1985 the discovery of the football like structure of C_{60} was reported based on the prominence of a peak observed at m/z = 720 in the mass spectrum of laser vaporized graphite [1]. Subsequently other fullerenes were proposed and these arrangements of carbon atoms were soon recognized as an entirely new and naturally occuring allotrope of carbon, in addition to well known graphite and diamond [2]. The laser vaporization experiments were initially undertaken because this was thought to be a way to produce linear carbon chain molecules in the laboratory and hopefully pave the way to obtain their electronic spectra. The main motivation behind the early studies came from the fact that the cyano-polyacetylenes were shown to be constituents of dense interstellar clouds by radioastronomy in the 1970's [3]. In the life-cycle of stars, these clouds are the precursors of new stars and they themselves arise from diffuse clouds which in turn have accreted dust grains and molecules from dying stars [4].

Whereas the dense clouds are opaque to visible radiation from stars the diffuse ones transmit this to a differing degree. In the spectra of stars observed through these clouds absorption features called the diffuse interstellar bands (DIBs) are found, as illustrated in Figure 1. The first DIBs were discovered over a hundred years ago [5] and with increasing sensitivity of optical detection they currently number around five hundred [6]. In view of the fact that diffuse clouds are the predecessors of dense clouds one might expect that the cyano-polyacetylenes or similar species are also present and could be among the molecules responsible for the DIBs.

The cyano-polyacetylenes are, however, closed shell molecules with singlet ground states and thus the electronic absorptions of the species detected in the dense clouds, the largest being $HC_{11}N$, will lie in the ultraviolet. In contrast the electronic configurations of some bare carbon chains contain unpaired electrons [7] and are expected to have absorptions in the visible, where the majority of DIBs are found. In 1977 Douglas proposed that not only the spectroscopic signature but also the photophysical properties of such carbon chains make them appealing candidates for some of the interstellar absorptions [8]. In the 1990's the electronic spectra of a selection of carbon chains and their ions were measured in the laboratory and compared with astronomical data [9]. The particular sizes proposed comprising up to a handful of carbon atoms have now been excluded as candidates for the DIBs [10].

Just two years after the discovery of C_{60}, now known by the name Buck-

minsterfullerene, H. W. Kroto brought its astrochemical importance to the forefront [11]. In his contribution to a meeting dealing with potential interstellar molecules he wrote: "The present observations indicate that C_{60} might survive in the <u>general</u> interstellar medium (probably as the C_{60}^+ ion) protected by its unique ability to survive processes so drastic that, most if not all, other known molecules are destroyed".

2   Spectroscopy of the fullerenes

The major breakthrough in fullerene chemistry took place in 1990 at the laboratory of W. Krätschmer where C_{60} was isolated in macroscopic amounts [12]. This development enabled R. Smalley's team to obtain the electronic spectrum of C_{60} in 1991. The gas phase spectrum was obtained by a resonant two colour two photon ionization method in a molecular beam of C_{60} produced by laser vaporization [13]. The measurements revealed a weak, vibrationally resolved, absorption system in the visible near 600 nm and much stronger, but very broad bands around 400 and 300 nm. Astronomers tried to detect C_{60} in the diffuse clouds based on these spectroscopic signatures [14, 15] but to date this has not been successful.

Laboratory studies of the electronic spectrum of the ions C_{60}^+ and C_{60}^- soon followed. The first experimental observation of the lowest energy electronic transition of C_{60}^+ was reported in 1992 by T. Shida's group [16]. The C_{60}^+ and C_{60}^- spectra were recorded in glassy matrices at 77 K, however, because this environment gives rise to broad absorptions the measurements were unsuitable for comparison with astronomical data. Prior to this publication experiments using neon matrices showed that this is the best medium, in the absence of gas phase data, to obtain vibrationally resolved electronic spectra of open-shell cations [17]. Our group was also involved in such studies, especially as our earlier gas phase emission spectra of organic cations in supersonic free jets [10] provided data on the expected neon to gas phase spectral shifts. These arise due the interaction with the matrix environment and tend to be in the range from 50 to $150\,\mathrm{cm}^{-1}$ toward the red in neon as compared to the gas phase for most $\pi - \pi$ excitations corresponding to the lowest electronic transitions of organic cations [9].

From the 1990 period onward our strategy to detect the electronic transitions of larger organic cations, anions and neutral radicals was to locate and identify these first *via* absorption spectra in 5 K neon matrices and with

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this information in hand carry out the measurements in the gas phase using a number of sensitive laser based techniques. By 1989 we had developed an approach that enables deposition of mass-selected species, cations or anions, that significantly improved the versatility of the neon matrix isolation experiment [18]. The corresponding neutral molecules can be subsequently generated from the mass-selected ions *in situ*. This strategy has ultimately allowed the electronic spectra of linear carbon chains, their anions and derivatives including hydrogen, nitrogen [9] and recently oxygen [19], to be measured in the gas phase. Such species are of relevance not only to interstellar space, but also in combustion and as reactive intermediates in organic chemistry.

The availability of a C_{60} sample allowed us to obtain vibrationally resolved electronic spectra of C_{60}^+, C_{60}^- [20], C_{70}^+ and C_{70}^- [21] in neon matrices in 1993. The aim was to use this information to measure the electronic spectra of these species in the gas phase under similar cold conditions to those prevailing in diffuse clouds. The main motivation for the study was to record the electronic spectrum of C_{60}^+ and we wrote in the paper: "Thus the origin of the C_{60}^+ gas-phase transition should lie in the $965 - 951$ nm range. However, spectral observations of diffuse interstellar bands are presently not available at these wavelengths".

Presumably these neon matrix results and the gas phase wavelength prediction led B. Foing and P. Ehrenfreund to look for DIBs in this spectral range. In 1994 they reported the identification of two DIBs that are close in wavelength to the first two absorption bands of C_{60}^+ observed in a neon matrix. This led them to propose that these are caused by the absorption of C_{60}^+ ions in diffuse clouds [22]. It was subsequently pointed out that if this attribution is correct, it is unusual that the energy shifts from the neon matrix to the gas phase are both small and irregular: $14\,\mathrm{cm}^{-1}$ for the 9632 DIB whereas only $7\,\mathrm{cm}^{-1}$ for the 9577 DIB. Thus it was concluded that only a gas-phase spectrum of C_{60}^+ at low temperature will resolve this problem [23]. A comparison between the matrix spectrum and the astronomical data is shown in Figure 2; as can be seen the match is not entirely convincing, also due to the much broader widths of the neon matrix absorptions that are caused by solid state effects. There followed several further astronomical studies that confirmed the interstellar nature of the near infrared absorptions [24, 25, 26] but were unable to prove they are due to C_{60}^+ in the absence of a gas phase laboratory spectrum. It took our group over 20 years to achieve this and the following outlines the concepts, difficulties and final success in 2015.

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3 Towards the gas phase spectrum of C_{60}^+

3.1 Challenges & Techniques

The diffuse interstellar clouds are extremely low pressure, cold and hostile environments that are subjected to a high radiation field. Their abundance is dominated by hydrogen which can exist in both atomic and molecular form. Under these conditions a molecule will collide with H or H_2 about once a year and thus relaxation by infrared emission, occurring on a millisecond timescale, is a major pathway to cool the internal degrees of freedom [27]. However, because the lifetimes of such diffuse interstellar clouds may be a million years, the rotational and vibrational degrees of freedom of the molecules present are equilibrated to a low temperature. Diatomic species with a dipole moment are able to attain $2.7 \, \text{K}$ in the diffuse medium through the spontaneous emission of photons. This spectroscopic observation was an early indication of the cosmic microwave background [28]. However, molecules without a permanent dipole moment reside at somewhat higher temperatures [6]. For example, cyclic H_3^+ was detected in the diffuse clouds by its infrared transitions [29] and found to have a rotational temperature of $50 - 80 \, \text{K}$. A similar temperature was inferred for the non-polar linear chain C_3 based on its electronic spectrum [30].

Supersonic free jets have been traditionally used to record the spectra of gas phase molecules. With such techniques the rotational degrees of freedom are readily relaxed, even to temperatures below $1 \, \text{K}$. However, due to the limited number of collisions in the expansion the vibrations are not so efficiently cooled [31]. In our earliest studies of the electronic transitions of open-shell organic cations, the emission spectra observed by electron impact ionization of seeded molecular beams also indicated inefficient relaxation of vibrational modes [32]. Thus it was decided to use a method in which collisional cooling equilibrates the internal degrees of freedom. The adopted approach was to store mass-selected cations in a radiofrequency (RF) trap where the ions are cooled *via* collisions with helium atoms at cryogenic temperatures. The initial experiments utilized a 22-pole RF trap according to the design [33] and pioneering work of D. Gerlich [34]. At the buffer gas pressures used the trapped ions typically undergo a collision every microsecond. With sufficiently long trapping periods the required low temperature can be attained even for molecules with a large number of degrees of freedom. This has been proven in our measurement of known electronic spectra of radical cations,

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such as that of diacetylene [35]. A schematic of the current ion trapping apparatus is shown in Figure 3.

The number of ions stored in a RF trap, typically some thousand, precludes direct absorption measurements based on the attenuation of light according to the Beer-Lambert expression $I = I_0 \exp(-\sigma nl)$. Thus in order to measure the electronic spectra an alternative approach to detect the absorption of a photon must be adopted. One method is action spectroscopy whereby the electronic transition of interest is first induced by one laser wavelength and the absorption of a second, higher energy, photon results in the fragmentation of the molecular ion. Both the parent and fragment ions are held in the trap and upon their extraction a mass-selecting device counts the fragment ions produced. The absorption process can thus be followed by monitoring the number of product ions as a function of the wavelength of the first laser. This approach has worked well for a number of open-shell cations, especially the polyacetylenes [36]. However, it is not a general approach as it relies on the dynamics of the excited electronic state. When using pulsed lasers this dictates whether nano-, pico- or femtosecond systems should be used. The absorption bands of species with excited state lifetimes in the femtosecond range are too broad to be of relevance to the DIBs. Nevertheless, as the excited electronic state lifetimes of large molecules are intrinsic, efforts to record their electronic spectra by tuning both the wavelength and time delay between laser pulses is a daunting task.

A second restriction is well known from electron impact ionization experiments in the field of mass-spectrometry. In order to induce fragmentation rates in microsecond range for large molecules, ionization with energies well in excess of the dissociation threshold are used. In standard mass-spectrometry $70\,\mathrm{eV}$ electron impact achieves this. Broadly considered, the larger the species the more readily is the excess energy above the fragmentation threshold redistributed among the internal degrees of freedom and the slower the rate. This is the realm of statistical theories of unimolecular dissociation. An additional handicap is that the Franck-Condon factors for the dissociation step get smaller as one moves further from the energetic threshold.

The problems caused by the individuality of large molecules can be illustrated by taking the example of coronene, $C_{24}H_{12}^+$, and protonated coronene, $C_{24}H_{13}^+$. It was possible to record the electronic spectrum of $C_{24}H_{13}^+$ with a resonant visible photon absorption followed by irradiation at $266\,\mathrm{nm}$ in order to detach the hydrogen atom and monitor the production of $C_{24}H_{12}^+$

ions [37]. However, such a scheme was not successful for coronene cation $C_{24}H_{12}^+$ itself [38]. In the case of C_{60}^+ fragmentation occurs *via* the loss of C_2 units and in order to achieve a rate of a few ions per millisecond the C_{60}^+ internal energy needs to be significantly in excess of the threshold, in the range $20-30\,\mathrm{eV}$ [39], dictating the use of an X-ray laser.

We therefore decided to develop a general method which relies on the scanning of just one laser colour, is independent of the lifetime of the excited electronic state and is sensitive enough to use with merely several thousands of ions held in the radiofrequency trap. The approach which succeeded is based on inhibiting the formation of the weakly bound helium complexes with molecular ions that can be formed *via* three body collisions [40]. Due to their small binding energy the prerequisite for the formation of helium complexes is that the internal temperature of the ion is low. The basis of the experiment is to measure a change in the number of complexes produced in the trap following electronic excitation of the bare molecule ion.

This was demonstrated by recording of the electronic spectrum of N_2^+ [40]. The well studied $A\,^2\Pi_u - X\,^2\Sigma_g^+$ electronic transition has precisely known individual rotation lines and thus whether the spectrum of the bare N_2^+ ion or that of the complex $N_2^+ - $He is being recorded can be unambiguously distinguished. In this work the spectrum of the $N_2^+ - $He complex itself was not observed, presumably because the excited state of the complex is so short lived that the rotational lines are smeared out as result of Heisenbergs uncertainty principle. The method appears to be generally applicable as subsequent use of this to record transitions between vibrational levels in the infrared have shown [41].

3.2 Spectroscopy of C_{60}^+ below $10\,\mathrm{K}$

These activities set the stage to attempt gas phase spectroscopic measurement of C_{60}^+ at temperatures below $10\,\mathrm{K}$. The first step towards this goal was to produce $C_{60}^+ - $He complexes in the low temperature trap by three body collisions:

$$C_{60}^+ + 2\mathrm{He} \quad \rightarrow \quad C_{60}^+ - \mathrm{He} + \mathrm{He} \tag{1}$$
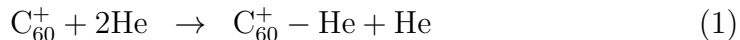
By operating the experiment at a temperature of $5\,\mathrm{K}$ and with a helium number density of $10^{15}\,\mathrm{cm^{-3}}$, $C_{60}^+ - $He complexes were readily formed.

It was decided that following the *in situ* production of $C_{60}^+ - $He complexes, gas phase spectroscopic information could be obtained using a simple alter-

native approach. Due to the low binding energy of the complex ($\sim 100\,\mathrm{cm^{-1}}$) absorption of a near infrared photon ($\sim 10400\,\mathrm{cm^{-1}}$) leads to dissociation by the loss of the helium atom. This is a known method commonly used in the infrared region to study the structure of ionic complexes [42]. In 1989 our group used this approach to record the electronic spectrum of $N_2^+ - He$ [43]. The spectrum was found to be superimposable with the $B\,^2\Sigma_u^+ - X\,^2\Sigma_g^+$ spectrum of the bare N_2^+ ion itself. These results, obtained using a $0.5\,\mathrm{cm^{-1}}$ bandwidth pulsed laser, indicated that the perturbation on the electronic spectrum of N_2^+ induced by the presence of the helium atom results in a shift in the transition energies of less than $1\,\mathrm{cm^{-1}}$. Although $N_2^+ - He$ complexes were readily produced in a supersonic expansion, the production of a beam of C_{60}^+ ions with such a low internal temperature to allow formation of $C_{60}^+ - He$ complexes is significantly more challenging. The difficulty involved in achieving relaxation of all of the C_{60} vibrational modes to their ground states was discussed recently [31]. In our ion trapping experiments $C_{60}^+ - He$ formation is only detected after collisional relaxation of both the rotational and vibrational degrees of freedom to around $6\,\mathrm{K}$.

4   Gas phase measurements

4.1   First identification of DIBs

The spectrum of $C_{60}^+ - He$ recorded in the ion trap resembles the absorptions of C_{60}^+ in the neon matrix, revealing the origin band at $9632.7\,\text{Å}$ and an adjacent band to higher energy at $9577.5\,\text{Å}$ [44], as shown in Figure 4. Furthermore, two other weaker transitions some $200\,\mathrm{cm^{-1}}$ to higher energy were also observed. It became immediately apparent that within the uncertainty of the astronomical measurements the two DIB absorptions coincide in wavelength with the laboratory spectrum of $C_{60}^+ - He$. The precise wavelength of the 9632 DIB reported in various astronomical studies is a somewhat delicate issue because an overlapping Mg II line has to be subtracted in order to reveal the DIB contour. A more detailed comparison showed that the width of the laboratory and DIBs are similar, with full-width-at-half-maximum (FWHM) of around $2.5\,\text{Å}$, and that the relative intensities of these two laboratory absorptions and those in the interstellar spectrum also agree within the errors of the two measurements. This then led to the conclusion that indeed the 9632 and 9577 DIBs are due to C_{60}^+, as proposed in the early 1990's [22]. For astro-

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nomical purposes the electronic spectrum of $C_{60}^+ - He$ can be viewed as that of C_{60}^+ after taking into account a small $0.7\,\text{Å}$ shift in the band wavelength caused by the helium atom.

The structure of C_{60}^+ is reduced from the high I_h symmetry group of neutral C_{60} because of Jahn-Teller distortions, although the effect is small for quite a rigid molecule. Theoretical calculations predict that the ground state of C_{60}^+ in D_{5d} and D_{3d} symmetries have similar energies [45, 46]. In the original matrix absorption study reported in 1993 [20] it was suggested that the two strongest absorptions are the origin bands of two such isomers of C_{60}^+, e.g. of D_{5d} and D_{3d} symmetries, both stabilized in the frozen neon matrix. An alternative explanation was that the $9577.5\,\text{Å}$ and $9632.7\,\text{Å}$ absorption bands arise as a result of two excited electronic states close in energy and that only the lowest energy isomer is present in the neon matrix. Included in this discussion is also the possibility that the two states are the spin-orbit components of a degenerate ^2E state [47]. Measurements in the ion trap reveal that both absorption bands originate from just one isomer [44]. This follows because irradiation of the ion cloud at either $9577.5\,\text{Å}$ or $9632.7\,\text{Å}$ leads to the destruction of all $C_{60}^+ - He$ complexes stored in the trap. Thus the $9632.7\,\text{Å}$ band is the origin of the $^2E_{1g} - X\,^2A_{1u}$ (D_{5d} symmetry) system and the $9577.5\,\text{Å}$ absorption appears to be a transition to the next excited electronic state, also $^2E_{1g}$ symmetry, which lies just $60\,\text{cm}^{-1}$ to higher energy.

The laboratory measurement is on $C_{60}^+ - He$ ions with a rotational temperature of around $6\,\text{K}$. This is readily established because the internal temperature is given by the mass-weighted average of the translational temperature of the ions (mass m_1) and the helium buffer gas (mass m_2) [48]. The latter is determined by the $5\,\text{K}$ temperature of the trap walls. The formula $T_{rot} = (m_1 T_2 + m_2 T_1)/(m_1 + m_2)$ indicates that even for a high $150\,\text{K}$ translational temperature of $C_{60}^+ - He$, the rotational temperature is just $6\,\text{K}$. Neglecting the role of the helium atom, the absorption width contains contributions from the C_{60}^+ rotational envelope (FWHM_{rot}) and the excited state lifetime (FWHM_{int}). Simulations of the band profiles have been carried out for an electronic transition of C_{60} [49] and indicate that the width of the bands due to the rotational profile at $6\,\text{K}$ is only $\sim 1\,\text{Å}$. This implies an excited state lifetime of around $2\,\text{ps}$ because the total FWHM of $2.5\,\text{Å}$ is given by $(\text{FWHM}_{rot}^2 + \text{FWHM}_{int}^2)^{1/2}$. After absorption of the near infrared photon the electronic energy of around $1.3\,\text{eV}$ is redistributed among the rovibrational levels within the ground electronic state following an internal conversion process taking place on this timescale. This information also

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suggests that the internal temperature of C_{60}^+ in diffuse interstellar clouds appears not to be much higher than $30\,K$ because the two DIBs have FWHM of approximately $3\,\text{Å}$. However, it should be noted that other factors such as multiple overlapping clouds sampled along a particular line of sight may contribute to the DIB widths.

4.2   Additional C_{60}^+ DIBs

As a follow up to the identification of the 9632 and 9577 DIBs as absorptions of C_{60}^+, several aspects of the laboratory and astronomical spectra were confronted after this publication in 2015. In the laboratory measurement of additional absorption bands were undertaken [50]. As in the neon matrix spectrum there are three distinct absorptions to higher energy of the origin band (lower panel, Figure 5). Their relative intensities were determined and according to these results it was apparent that, in addition to the $9577.5\,\text{Å}$ and $9632.7\,\text{Å}$ absorptions, these three weaker C_{60}^+ bands should also be detectable as DIBs. A specific astronomical search was undertaken in collaboration with the astronomers G. A. H. Walker and D. Bohlender and indeed led to the observation of DIBs at the expected wavelengths, with consistent FWHM and relative intensities [51].

Parallel to these activities laboratory efforts were made to more precisely quantify the shift to the wavelengths of the C_{60}^+ bands that are caused by the helium atom in the measured $C_{60}^+ - He$ spectrum [52]. This was achieved by spectroscopic measurement of the two origin bands of $C_{60}^+ - He_n$, with $n = 1 - 3$. The electronic spectra of C_{60}^+ with multiple helium atoms attached could be obtained after achieving lower temperatures in the cryogenic ion trapping apparatus than used in the 2015 measurements. The results led to the conclusion that each of the helium atoms attached to C_{60}^+ induces a $0.7\,\text{Å}$ wavelength shift (Figure 6) and thus the wavelengths of the first five C_{60}^+ absorptions are predicted to lie at 9348.4, 9365.2, 9427.8, 9577.0, and 9632.1Å with a $\pm\,0.2\,\text{Å}$ uncertainty. These experimental results are also in agreement with recently reported $C_{60}^+ - He_n$ ($n = 2 - 32$) photofragmentation spectra obtained using a helium nanodroplet experiment [53]. There are many other C_{60}^+ absorptions toward even higher energy (upper panel, Figure 5), however, these are too weak to be currently detectable in the astronomical spectrum. The assignment of all of the higher energy C_{60}^+ absorptions is a complex problem due to the couplings between the excited vibronic levels in addition to Jahn-Teller effects.

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The determination of DIB wavelengths, their FWHM and relative intensities in the astronomical spectrum is sensitive to a number of factors. These include the number of clouds observed along the line of sight towards a star, the temperature of these environments and the accuracy of the background corrections applied. The latter are needed to account for both overlapping stellar spectral features as well as those caused by absorbers in the atmosphere of the Earth. In the near infrared spectral region strong bands appear due to water absorption. The number of clouds traversed by the starlight can be determined by inspection of sharp atomic interstellar spectral lines. In the line of sight towards the star HD 183143, where the strong C_{60}^+ bands are responsible for a 10 % attenuation in the light intensity, there are two interstellar clouds. This is indicated by the observation of potassium absorption lines with different Doppler shifts, as shown in Figure 7. The 9632 and 9577 DIBs reported by B. Foing and P. Ehrenfreund [24] are shown in Figure 8. In order to compare these with the laboratory C_{60}^+ spectrum, both DIBs were fit using two Lorentzian profiles. The characteristics of the latter were constrained by the experimentally determined values. The intentsity ratio and wavelength separation of each Lorentzian pair were fixed according to the observations of the interstellar potassium lines shown in Figure 7. To obtain the best fits to the astronomical data shown in Figure 8 the central wavelengths and FWHM of the Lorentzian laboratory profiles were allowed to vary by the small uncertainties inferred from the experimental study [52]. A similar comparison is shown in Figure 9 for the weaker C_{60}^+ astronomical bands observed towards both HD 183143 and HD 169454. This provides unequivocal evidence that C_{60}^+ is present in the diffuse interstellar medium and that for the first time in the hundred year history of the DIBs five are identified [54].

4.3 C_{60}^+ abundance in diffuse clouds

In order to discuss the astronomical implications of the presence of C_{60}^+ in diffuse interstellar clouds, its abundance in these environments has to be determined. The latter is usually expressed in terms of the column density, $N(C_{60}^+)$, which can be calculated using the formula $N(C_{60}^+) = \frac{mc^2}{\pi e^2} \frac{EW}{\lambda^2 f}$. The equivalent width (EW) can be determined from the astronomical absorption band and the only unknown quantity needed to evaluate $N(C_{60}^+)$ is the oscillator strength of the transition, f. In the case of polyatomic molecules f is usually obtained by a quantum mechanical calculation of the transition

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moments, however, this is not feasable for very large species. In the case of C_{60}^+, only low level calculations such as TD-DFT have been used. The two theoretical results reported in the literature lead to an estimate of the oscillator strength for the 9577 Å band of around 0.02 [45, 46]. In order to obtain this value the theoretical result, calculated for the electronic transition as a whole, is weighted according to the Franck-Condon factors of the vibrational bands in the spectrum. A similar result was deduced from recent absorption measurements in a neon matrix [55].

The column density can also be determined directly from the intensity ratio of the astronomical band (I/I_0) and the absolute absorption cross-section, σ, through the Beer-Lambert expression $N(C_{60}^+) = \ln(I_0/I)/\sigma$. A gas phase value of σ was obtained through ion trapping measurements [50]. The experimentally determined absorption cross-section of $5 \times 10^{-15}\,\mathrm{cm}^2$ at 9577Å, corresponding to $f \sim 0.02$, implies a column density of C_{60}^+ in the diffuse clouds of $2 \times 10^{13}\,\mathrm{cm}^{-2}$ towards the star HD 183143. This is comparable to the column density of the diatomic molecule CH^+ along this line of sight [29] with $N(H_3^+)$ just an order of magnitude larger [56].

4.4   Astronomical implications

The column densities of molecules present in the diffuse clouds decrease sharply with increasing size (see, for example, Tables 2 and 3 in Ref [6]). This observation, together with the relatively large value determined for C_{60}^+ has important implications for the processes that must set the organic inventory in these environments. In particular, as recently emphasized by Oka & Witt [57], there is a renewal of interest in top down chemistry. In this scenario the abundance of molecules is not determined by facile reactions of smaller components but rather through their ability to withstand decomposition in the long lifetime of diffuse clouds. In addition to C_{60}^+ being responsible for the first identification of a DIB carrier, its presence in these environments has important consequences for the transport of carbon from dying stars to diffuse clouds to dense clouds and then in new star formation [5]. The idea that C_{60}^+ and related fullerenes may play a role as precursors for the complex smaller molecules identified by radioastronomy in dense clouds, including the polyacetylene chains [3], now comes to the forefront.

The detection of C_{60}^+ in diffuse clouds leads to the question of the degree of ionization in this environment. The absorption features of neutral C_{60} have been searched for in the astronomical spectrum but so far without

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success [14, 15, 58]. Based on a lack of detection of C_{60} absorption bands in the UV, Herbig put an upper of $4.5 \times 10^{11}\,\text{cm}^{-2}$ on its column density [14]. This would imply that the degree of ionization in diffuse clouds is around 98 %. However, this estimate may be invalid because the UV absorptions are broader than the width used to derive the $N(C_{60})$ upper limit. C_{60} also has much narrower absorption bands in the 6000 Å region [13], where several weak DIBs (EW $\simeq$ 10 mÅ) have been observed (see discussion in [59]). Even if one of these C_{60} absorptions corresponds to a DIB with EW $\sim$ 10 mÅ then the degree of ionization would be 90 %; otherwise it is larger.

Though C_{60} has not been detected in the diffuse medium, in 2010 it was observed in the planetary atmosphere of a dying carbon star *via* its four characteristic infrared bands in emission [60, 61]. Since this discovery C_{60} has been found in a number of planetary nebula (Ref [62], and references therein), again through observation of its simple vibrational spectrum. This leads to intriguing questions of how C_{60} is formed in the nebula of evolved stars, and whether it is then transported to the diffuse interstellar clouds and ionized by the harsh radiation field to produce the high abundance of C_{60}^+. One suggestion is that C_{60} could be formed through the decomposition of larger graphitic and PAH like structures that are believed to be responsible for around 10 % of the cosmically available carbon [63]. Further open questions include whether the C_{60}^+ observed in diffuse clouds is neutralized during the formation of dense clouds and if C_{60}, C_{60}^+, and related fullerene derivatives could be a source, through decomposition due to high energy cosmic and X-ray radiation, of the complex molecules detected *via* radioastronomy in this environment.

4.5   Other fullerenes

Due to the remarkable stability of the carbon cage structure, the electronic spectra of other fullerenes are of interest in the context of the DIBs. Typically, the next most abundant fullerene produced by electric discharge or through laser vaporization is C_{70}. Similar to C_{60}, its low ionization potential of around 7.5 eV indicates that it could be formed in diffuse clouds. The absorption spectrum in a 5 K neon matrix was recorded in the early 1990's and found to contain electronic transitions in the spectral range of interest for the DIBs [21]. Gas phase laboratory measurements were recently made in a cryogenic ion trap by photodissociation of $C_{70}^+ - $He [50]. The lowest energy electronic transition of C_{70}^+ consists of a complicated pattern of around 20

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overlapping features of roughly equal intensity (Figure 10). In contrast, the electronic spectrum of C_{60}^+ is dominated by the two absorptions at $9632\,\text{Å}$ and $9577\,\text{Å}$ which carry most of the electronic band oscillator strength. The dilution of the oscillator strength across many absorption bands in the case of C_{70}^+ hinders astronomical detection and to date no C_{70}^+ DIBs have been identified.

A more quantitative comparison with the C_{60}^+ spectrum can be made by considering the absorption cross-sections of the individual absorption bands [50]. The cross-section at the origin band of the electronic transition of C_{70}^+ ($7959\,\text{Å}$) is measured to be $7 \times 10^{-18}\,\text{cm}^2$, nearly three orders of magnitude smaller than for C_{60}^+ at $9577\,\text{Å}$. Thus it is not surprising that the corresponding C_{70}^+ DIBs have not detected. Even if C_{70}^+ would be present in the diffuse clouds with the same abundance as C_{60}^+, the much smaller absorption cross-sections preclude its detection. It is worth noting that neutral C_{70} has been detected *via* infrared emission in the young planetary nebula Tc 1 alongside C_{60} [60].

Another relevant species to consider is C_{60}^{2+}. The process $C_{60}^+ \rightarrow C_{60}^{2+}$ requires $\sim 11.5\,\text{eV}$, which is less than the $13.6\,\text{eV}$ energetic threshold of photons in the diffuse medium that is determined by the ionization potential of hydrogen atoms. As a result, one might also expect C_{60}^{2+} to be present in diffuse clouds. However, its ground electronic state is a singlet, $^1A_1$, and thus the electronic transitions lie in the ultraviolet. The C_{60}^{2+} spectrum has been observed in neon matrices and shows very broad absorptions near $4000\,\text{Å}$ and to shorter wavelengths [55]. The large FWHM of these bands, however, hinders the identification of this species in diffuse clouds. Although C_{70}^+ and C_{60}^{2+} do not possess appropriate electronic transitions to allow detection in diffuse clouds, the electronic spectra of other fullerene cations are sought, especially in light of the current discussions on a top down formation processes [57]. Of particular interest are the fragmentation products of C_{60}^+ produced under interstellar conditions.

Hydrogen is the dominant element in the universe with a relative abundance of 90%. The remainder is made up of mostly He ($9\,\%$) with C, N and O being just 10^{-4} in fractional abundance. Thus as C_{60}^+ is present in the diffuse interstellar medium, the role of hydrogenated derivatives of C_{60}^+ has to be addressed. In the case of neutral C_{60} a distribution of derivatives have been chemically synthesized, usually with the $C_{60}H_{18}$ and $C_{60}H_{36}$ species dominating. For each $C_{60}H_n$ species there will be numerous isomers [64]. A similar situation will prevail for the $C_{60}^+H_n$ derivatives and thus even with

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mass-selection, their electronic and infrared absorption spectra may consist of a superposition of signals due to the different structures. It remains to be seen whether a subset of these isomers is preferentially produced and able to survive in the ISM so their fractional abundance is large enough to allow astronomical detection. Kroto and Jura [65] have argued that, in addition to the possibility of fullerene derivatives with cosmically abundant metals being candidates for the DIBs, C_{60}^+H may be the most abundant fullerene derivative on the basis of the abundance of small protonated species such as HCO^+. The electronic spectrum of C_{60}^+H has been observed in solution and contains broad absorption bands unlike the sharp features of C_{60}^+ in the near infrared [66]. Thus, although C_{60}^+H will be present in the diffuse clouds the lack of a distinct spectroscopic signature may preclude its detection.

Acknowledgements

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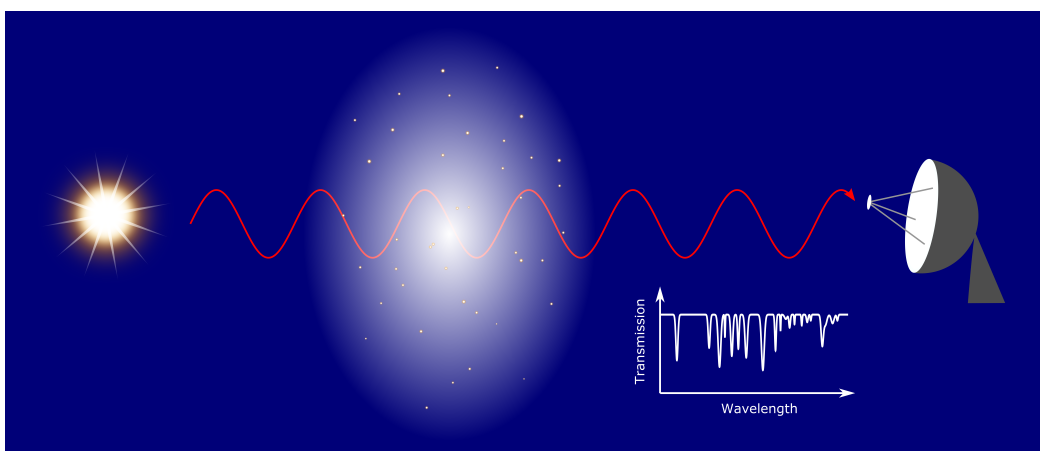
Figure 1: The diffuse interstellar bands are a set of around five hundred absorption features that are observed in the spectra of star light transmitted through interstellar clouds. They are believed to be caused by electronic transitions of polyatomic molecules present there. For the first time in the one hundred year history of this long standing astronomical enigma several absorptions have been assigned to the Buckminsterfullerene cation, C_{60}^+.
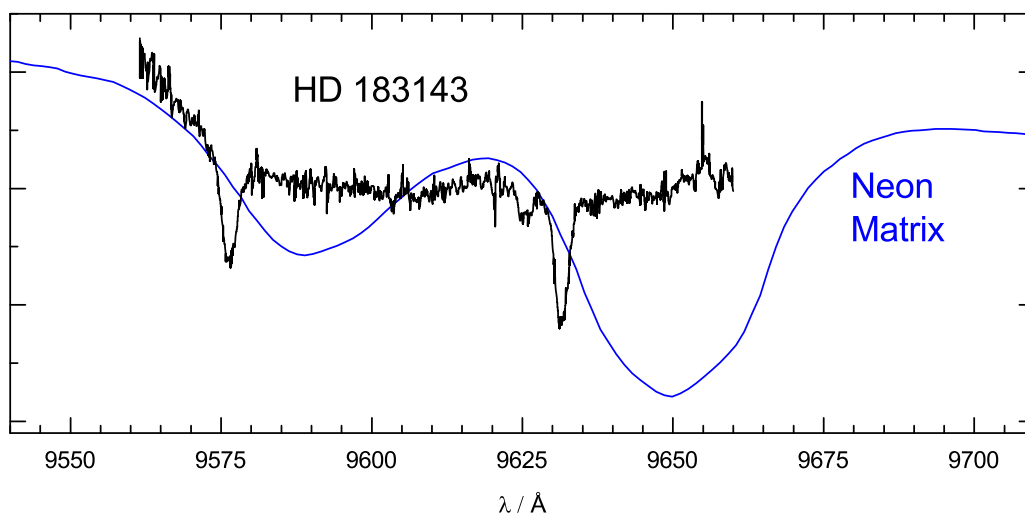
Figure 2: The two strongest bands in the $A\,^2E_{1g} \leftarrow X\,^2A_{1u}$ (assumed D_{5d} symmetry) electronic absorption spectrum of C_{60}^+ recorded in a neon matrix (blue) compared with astronomical observations towards the star HD 183143 (black). The latter is from [24] and is of higher signal-to-noise ratio than the original observations reported in [22].
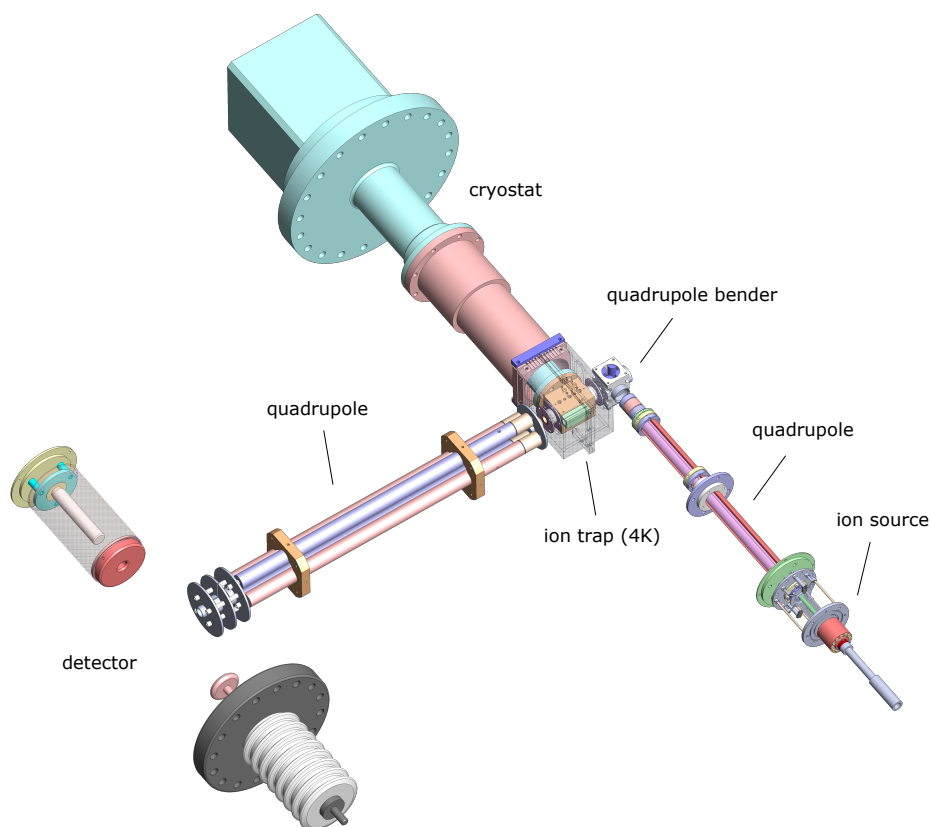
Figure 3: The cryogenic ion trap apparatus used to record the electronic spectra of cold molecular ions. Ions are produced by electron bombardment of the neutral gas. After passing through a quadrupole mass filter they are injected into a radiofrequency ion trap (22-pole or 4-pole). Here, the internal degrees of freedom of the hot ions are cooled *via* collisions with 4 K helium buffer gas. After interaction with laser radiation the stored ions are extracted and analysed using a quadrupole mass spectrometer and Daly detector.

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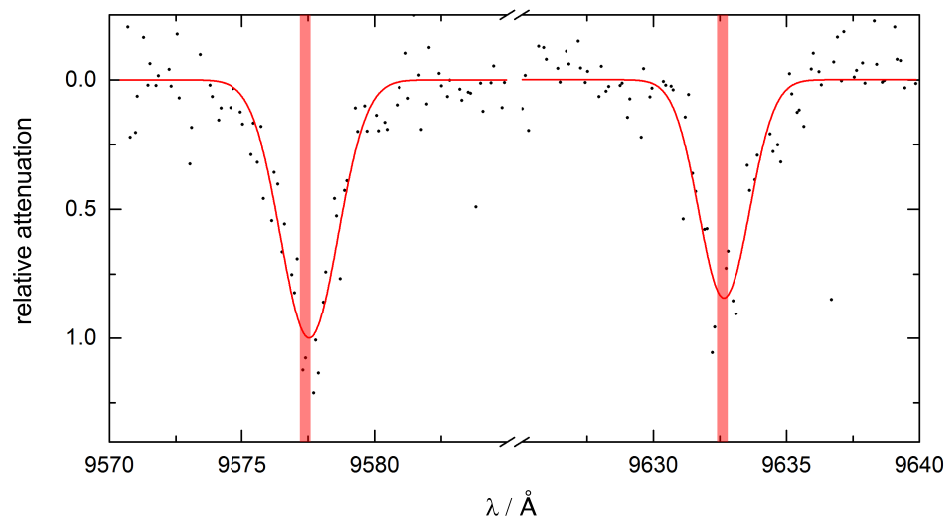
Figure 4: The two strongest bands in the 6 K gas phase electronic spectrum of $C_{60}^+ - He$. Gaussian fits to the experimental data (circles) are the red lines. The vertical lines are at the rest wavelengths of the C_{60}^+ DIBs reported in [25], their width indicates the given uncertainty.
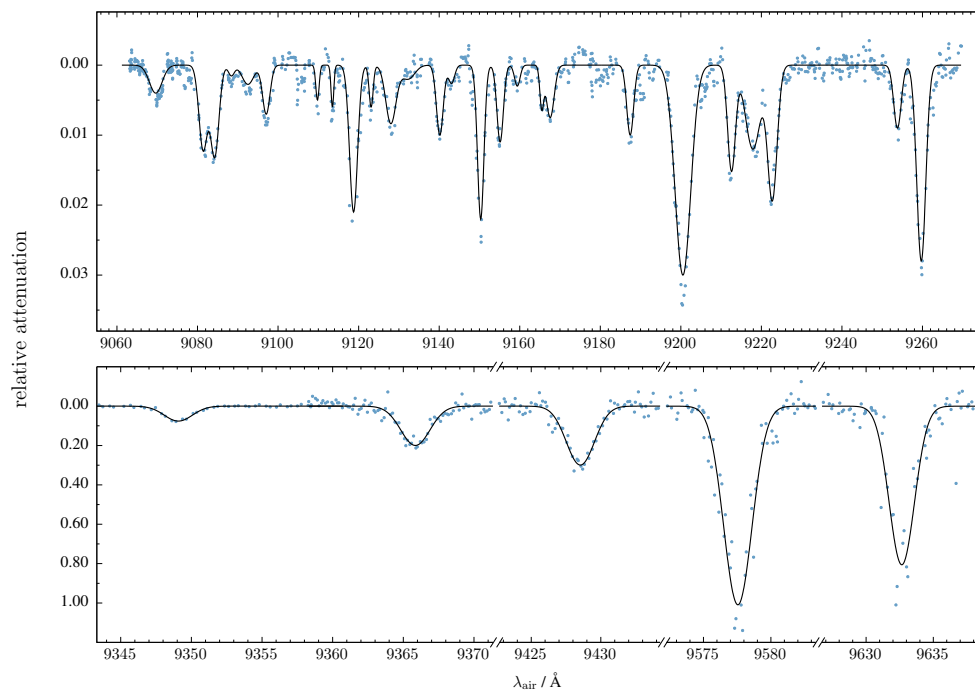
Figure 5: The 6 K gas phase spectrum of $C_{60}^+ - He$ in the range $9000 - 9650\,\text{Å}$ [50]. The intensities of the bands are scaled by the relative absorption cross-sections which are normalized to the strongest absorption near $9577\,\text{Å}$
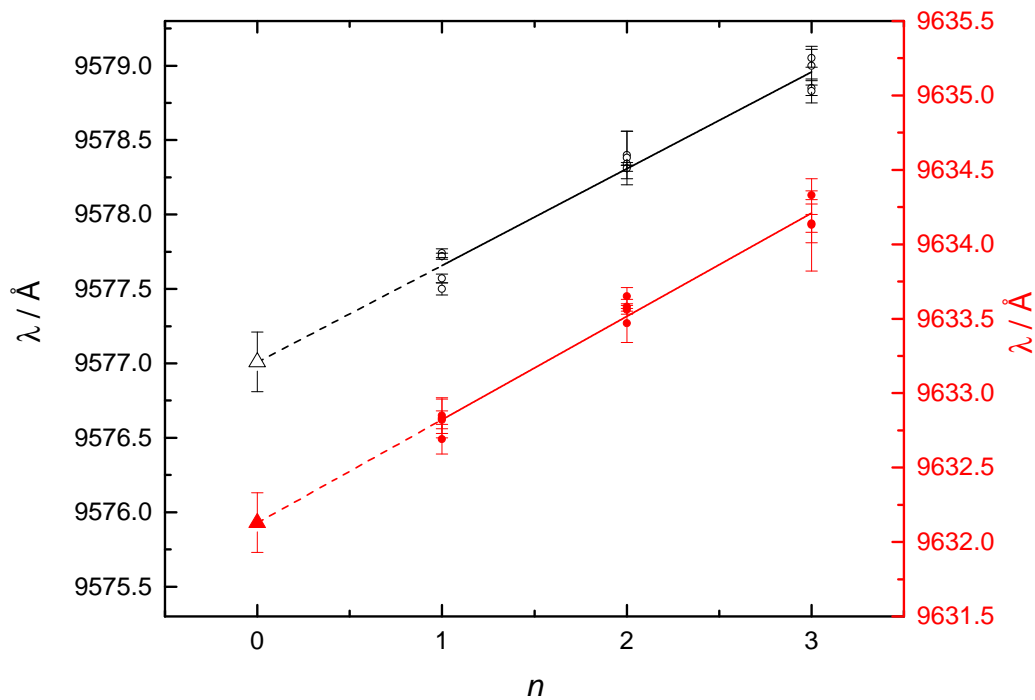
Figure 6: Wavelengths of the two strongest absorption bands in the electronic spectra of $C_{60}^+-He_n$ ($n = 1-3$) (symbols) [52]. The linear fits (lines) indicate a wavelength shift of $0.7\,\text{Å}$ per helium.
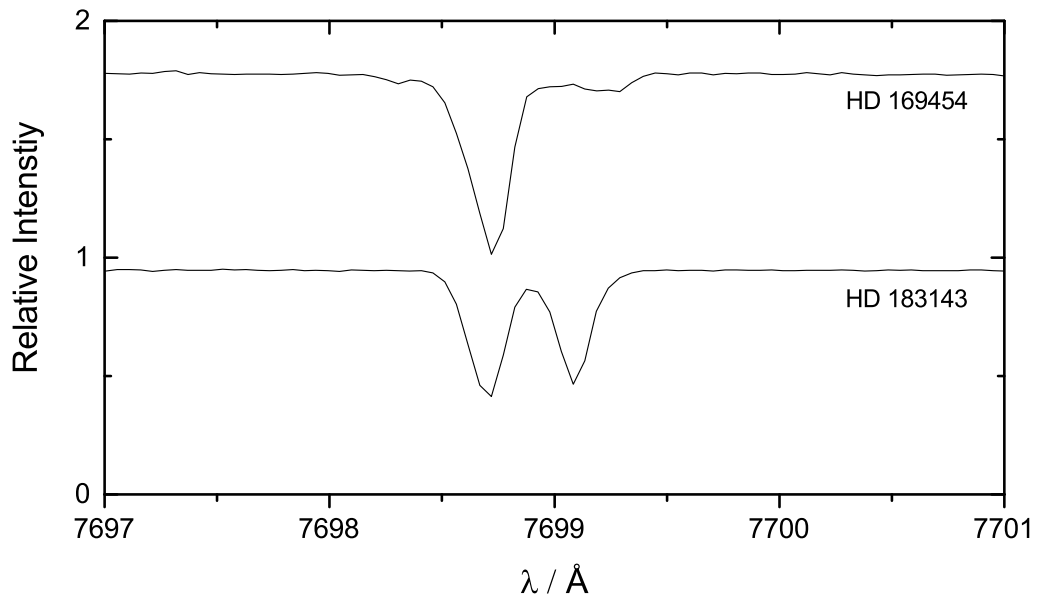
Figure 7: Potassium absorption line observed in the diffuse clouds towards the star HD 169454 (top) and HD 183143 (bottom) [54]. The offset from 7699.0 Å provides information on the radial velocity of the interstellar cloud(s). The lower trace indicates that two interstellar clouds with different radial velocities are sampled in this line of sight.
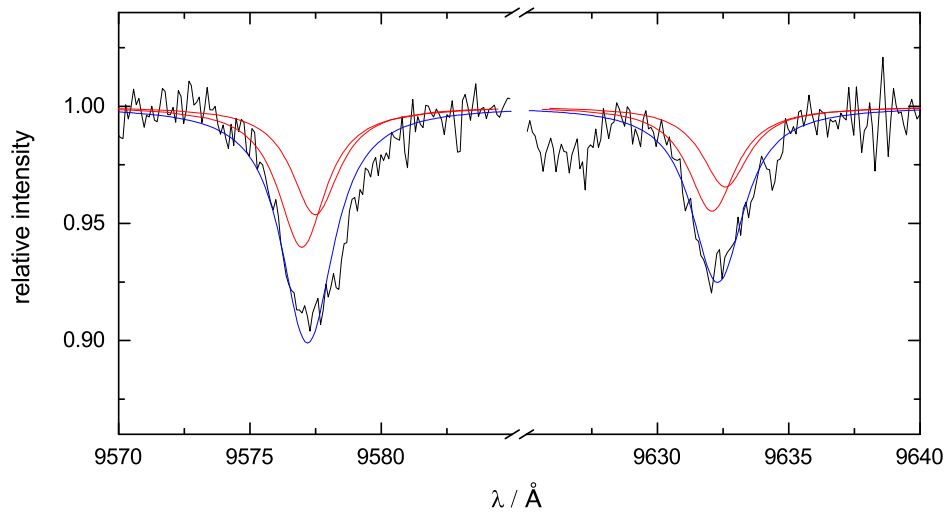
Figure 8: Fits (blue) to the DIBs (black) reported by B. Foing and P. Ehren-freund [24] after correction for the Mg II stellar line in the region of the 9632 DIB [54]. The red lines are Lorentzian profiles constrained by the extrapo-lated C_{60}^+ laboratory wavelengths (± 0.2 Å uncertainty). Each DIB is fit with two Lorentzians to account for the two interstellar clouds sampled along this line of sight.
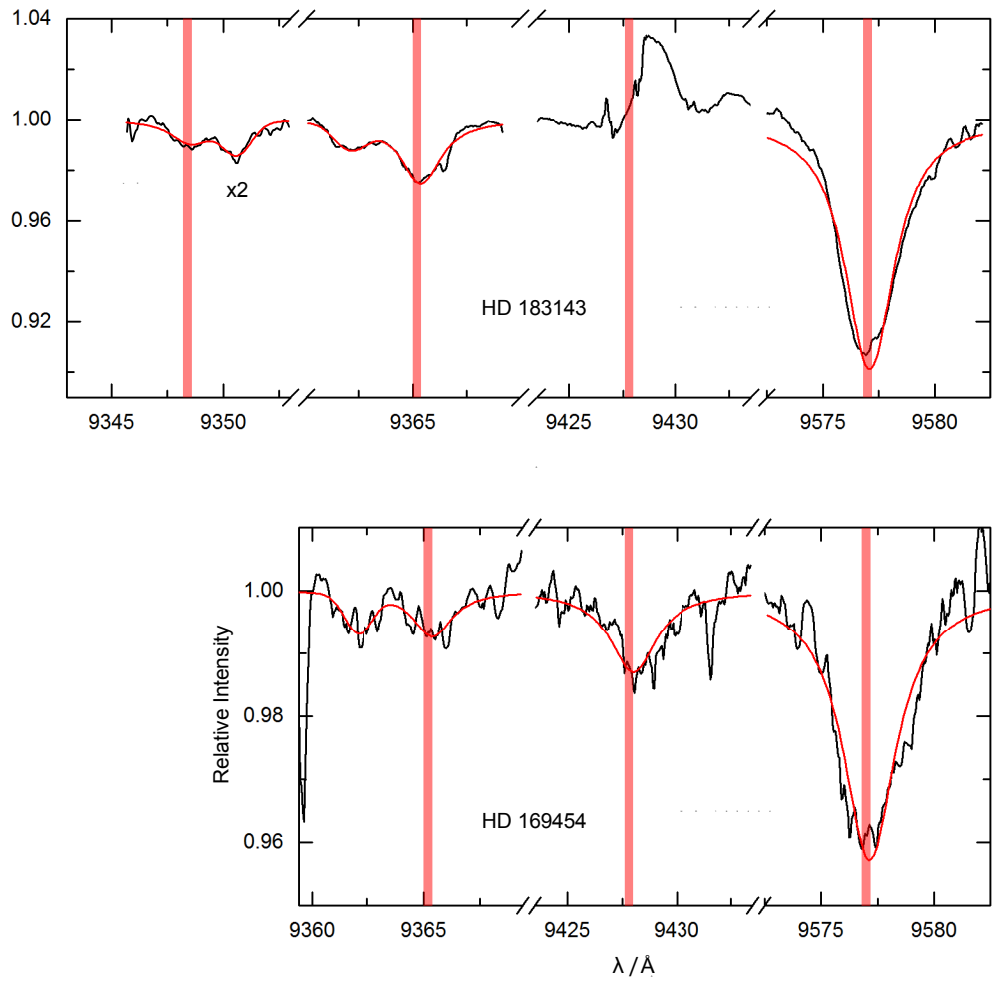
Figure 9: Astronomical observations towards HD 183143 (top) and HD 169454 (bottom) in the region of the laboratory C_{60}^+ absorption bands (vertical lines) [54]. Fits to the DIBs constrained by these wavelengths ($\pm 0.2\,\text{Å}$ uncertainty) are shown by the red lines. The weaker interstellar absorptions are close to the astronomical detection limits.
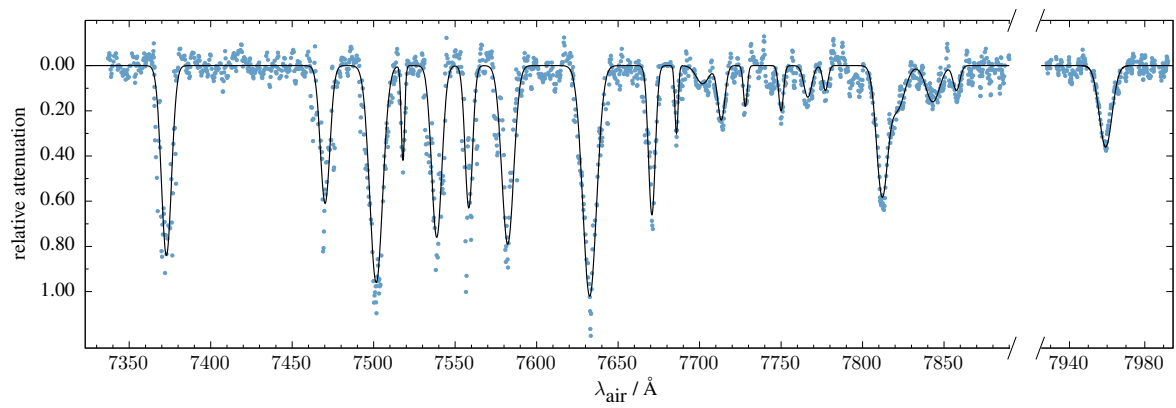
Figure 10: Gas phase spectrum of $C_{70}^+ - $ He below $10\,$K in the region $7300 - 8000\,$Å [50]. The spectrum corresponds to the lowest energy electronic transition, assigned as $^2E_1' \leftarrow X\,^2E_1''$ in D_{5h} symmetry.