

Perspective: C_{60}^+ and laboratory spectroscopy related to diffuse interstellar bands **F**

Cite as: J. Chem. Phys. **146**, 160901 (2017); <https://doi.org/10.1063/1.4980119>

Submitted: 21 February 2017 • Accepted: 29 March 2017 • Published Online: 24 April 2017

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Perspective: C_{60}^+ and laboratory spectroscopy related to diffuse interstellar bands

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(Received 21 February 2017; accepted 29 March 2017; published online 24 April 2017)

In the last 30 years, our research has focused on laboratory measurements of the electronic spectra of organic radicals and ions. Many of the species investigated were selected based on their potential astrophysical relevance, particularly in connection with the identification of appealing candidate molecules for the diffuse interstellar absorptions. Notably, carbon chains and derivatives containing hydrogen and nitrogen atoms in their neutral and ionic forms were studied. These data could be obtained after developing appropriate techniques to record spectra at low temperatures relevant to the interstellar medium. The measurement of gas phase laboratory spectra has enabled direct comparisons with astronomical data to be made and though many species were found to have electronic transitions in the visible where the majority of diffuse bands are observed, none of the absorptions matched the prominent interstellar features. In 2015, however, the first carrier molecule was identified: C_{60}^+ . This was achieved after the measurement of the electronic spectrum of C_{60}^+ -He at 6 K in a radiofrequency ion trap. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4980119>]

I. INTRODUCTION

A long standing riddle of astronomy is the origin of absorption features detected in the spectrum of reddened starlight, known as diffuse interstellar bands (DIBs).^{1–3} These arise due to unidentified species present in huge clouds of gas and dust that are ubiquitous in space. The first astronomical observations were reported a hundred years ago⁴ and soon after their interstellar nature was established.^{5,6} A review of the early history of the DIBs has been given.⁷ The essential features of these absorptions are that they show varying intensities, widths, and profiles, including a number with contours reminiscent of the unresolved rotational structure found in the electronic spectra of large molecules. Furthermore, each DIB appears to be similar, though with some variations towards different reddened stars both in our galaxy as well as in some external ones.⁸ Together with the absence of the expected light polarization behaviour from a solid state (dust grain) phenomenon, these observations have led to the consensus that gas phase molecules are the carriers. Currently about five hundred DIBs have been catalogued^{9,10} and their numbers are continually increasing because of improvements to detection sensitivity. However, in the 400–900 nm region, where the majority of DIBs are observed, only a few dozen of these are particularly prominent, absorbing 10%–30% of the intensity of star light. Figure 1 shows the profiles of several DIBs in the optical region following observations toward the star HD 183143.

This perspective article outlines the concerted efforts made in the last 20–30 years to measure in the laboratory for the first time the electronic spectra of the molecules considered as promising DIB candidates and is organised as follows. In Section II the motivation behind early spectroscopic studies is

outlined. Section III details the experimental data obtained on the specific classes of molecule considered as key candidates for the DIBs. Section IV describes gas phase experiments that led to the identification of C_{60}^+ as a DIB carrier and with this the astronomical implications.

II. BACKGROUND

The majority of DIBs are observed in the visible range of wavelengths and this has focused attention on open-shell species: ions of stable molecules and organic radicals. In the case of cations this was an extension of the research we had pursued earlier, the measurement of the electronic spectra of radical cations of unsaturated organic molecules, first in emission in supersonic free jets produced by electron impact¹¹ and then as laser excitation spectra and parallel to this in absorption in neon matrices.¹²

After the identification of polar carbon chains, especially those of the cyano-polyacetylenes, in dense interstellar clouds by radio-astronomy,¹³ the electronic spectra of related species with allowed transitions in the visible were sought. In the evolutionary cycle of stars, diffuse to dense clouds is the preceding step to new star formation and thus the type of molecules identified in dense clouds may also be related to the DIB carriers. From a spectroscopic perspective, it is important to realise that closed-shell species, an example being the cyano-polyacetylenes identified in dense clouds, have electronic transitions in the UV while those of their cations lie in the visible. The same considerations apply to the isoelectronic species of the latter, C_nH , which are open-shell in contrast to the closed-shell polyacetylenes. As an example, the approximately linear behaviour of the wavelengths of the electronic transitions of polyacetylene chains as a function of the number of carbon atoms is illustrated in Figure 2.

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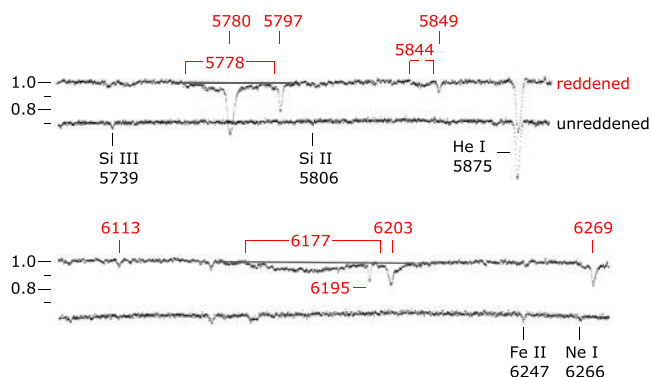


FIG. 1. Astronomical spectra obtained towards the reddened star HD 183143 (above) and the unreddened star B8 Ia β Orionis (below). The wavelengths of interstellar features (in Å) are given in red while those of atomic lines present in the spectra of unreddened stars are black. The horizontal lines across some of the DIBs indicate the continuum level. Reproduced with permission from G. H. Herbig, *Astrophys. J.* **196**, 129 (1975). Copyright 1975 American Astronomical Society.

An influential conjecture was made by Douglas who suggested that the expected photophysical properties of bare carbon chains C_n with $n = 5-15$ make them appealing candidates for the DIBs.¹⁴ It was argued that internal conversion following photon absorption leads to shortened excited electronic state lifetimes and hence widths that the DIBs exhibit. Bare carbon chains with an even number of atoms ($n > 2$) contain unpaired electrons and for a certain size their electronic transitions appear in the visible. Those with an odd number of atoms have closed shell ground electronic states with absorptions in the visible for $n > 15$. But the question was at which exact wavelengths do these lie. With this goal in sight, we embarked on a laboratory project to observe these transitions in the gas phase and thus be able to make a direct comparison with the astronomical data.

This took place in the preceding three decades. The obstacles in the search for unknown electronic spectra of transient species are (1) their preparation in sufficient concentration, (2) the availability of sensitive techniques for monitoring the absorption process, and (3) information on the wavelength range for the search. The solutions for these aspects were

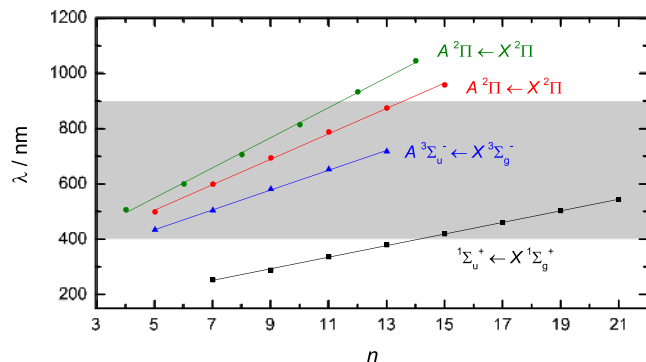


FIG. 2. Wavelengths of the origin bands of allowed electronic transitions of neutral (triangles) and positively charged (circles) polyacetylenes HC_nH and carbon chains C_n (squares) as a function of the number of carbon atoms, n . The green and red circles correspond to polyacetylene cations containing an even and odd number of carbon atoms, respectively. The shaded area is the wavelength range where the majority of DIBs are observed. Data are taken from Ref. 17.

provided as follows: (1) using supersonic free jets in conjunction with discharge and laser ablation sources, (2) with laser based approaches including resonant multi-photon processes, cavity ring-down spectroscopy, and ion traps, and (3) measuring the electronic spectra first in 6 K neon matrices using mass-selection.¹⁵

III. LABORATORY SPECTROSCOPY OF CANDIDATE MOLECULES

A. Carbon chains

Gas phase spectra of species present in dense clouds, $C_{2n}H$ ($n = 3-5$), as well as of some neutral carbon chains C_n ($n = 4, 5$), polyacetylenes $HC_{2n}H^+$, and their isoelectronic cyano-polyacetylene cations, were obtained in early laboratory studies by our group. All the comparisons with astronomical data yielded negative results but upper limits to the column density in the diffuse interstellar clouds of around $10^{11}-10^{12} \text{ cm}^{-2}$ were obtained.¹⁶ A list of such species, including many carbon anions, C_n^- , and a few cations, C_n^+ , can be found in a review.¹⁷ The only polyatomic identified in this astrochemical environment was C_3 via its $A^1\Pi_u-X^1\Sigma_g^+$ transition. Its column density was found to be in the range $1-2 \times 10^{12} \text{ cm}^{-2}$ depending on the cloud sampled.¹⁸ Interstellar absorptions due to C_4 and C_5 could not be detected¹⁹ nor those of the C_nH , HC_nH^+ , and HC_nCN^+ chains.¹⁶ These results led to the important conclusion that Douglas' hypothesis has to be modified: the carbon chains and related derivatives including H, N, or O and their ions of sizes up to a dozen of heavy atoms cannot be responsible for the stronger DIBs.²⁰ One anticipates that species such as C_6H , known constituents of dense clouds, will also be present in the diffuse clouds but with column densities $< 10^{11}-10^{12} \text{ cm}^{-2}$. In general, if molecules are in the diffuse clouds with such column densities, then the criterion for them being candidates for the strong DIBs is that their oscillator strengths have to be over an order of magnitude larger than the 10^{-2} values typical for species such as C_6H .

Long carbon chains with an odd number of atoms, C_{15} , C_{17} , $C_{19} \dots$, have large $f > 1$ oscillator strengths for their allowed ${}^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transitions in the visible (Figure 2). For example, C_{17} has an absorption at around 460 nm as the observed spectra in neon matrices have shown.²¹ The detection of their spectra in the gas phase has hitherto been unsuccessful. Either the concentration produced in the laser vaporization or discharge sources was too small or the lifetimes of their excited electronic states are too short, sub 100 fs due to internal conversion, to allow observation with the techniques used. The most appealing DIB candidates should satisfy the following criteria: in terms of their spectroscopic transitions, they should possess strong ($f \approx 1$) absorptions in the visible range, and with respect to their photophysics the excited states must have lifetimes longer than about 100 fs to be compatible with the typical DIB full-width-at-half-maximum (FWHM) of 0.1–10 Å. Whereas the first two requirements are experimentally and theoretically accessible, the dynamical characteristics of excited electronic states are molecule specific and difficult to predict using *ab initio* calculations.

As the diffuse medium is permeated by starlight up to 13.6 eV, the ionization potential of H, the degree of ionization may be high and astrochemical models have also indicated this.²² Thus the laboratory measurement of the electronic spectra of seemingly relevant open-shell organic cations was pursued as well. This followed naturally the data we obtained 30–40 years ago on the hundred or so cations which fluoresce.¹¹ Those which do not require the application of alternative techniques to detect the absorption process. Cavity ring down measurements using pulsed and continuous supersonic expansions with slit nozzles through which a discharge runs were successful for some ions; these include the astrophysically relevant polyacetylene cations, HC_{2n}H^+ ($n = 2-4$), and their isoelectronic cyano derivatives, $\text{HC}_{2n}\text{CN}^+$ ($n = 1-3$).

For other species, an ion trap apparatus was constructed and action spectroscopy was employed, specifically to record the absorptions of the longer polyacetylene cations up to HC_{16}H^+ ²³ and the protonated species $\text{H}_2\text{C}_{2n}\text{H}^+$ ($n = 2, 3$).²⁴ A schematic of the current ion trapping apparatus is shown in Figure 3. In this approach 10^3-10^4 buffer gas cooled ions are held in a radiofrequency (rf) trap where one tunable laser is used to search for the electronic transition of interest and a second fixed frequency laser of higher energy is used to fragment the electronically excited ions. The fragments are subsequently mass-selected and detected in order to record the spectrum. The comparison of these experimental results with the astronomical data led to upper limits of $10^{11}-10^{12}\text{ cm}^{-2}$ for the longer polyacetylene cations.

A significant development in the context of chain candidates has been the insight gained recently through the analysis of certain DIB profiles by Oka *et al.*^{25,26} This work was motivated by the observation that a few of the astronomical bands exhibit extended tails to the red (ETR) along a rather unique line of sight toward Hershel 36.²⁷ In these unusual clouds, and in contrast to the other sightlines investigated, absorption by rotationally excited CH and CH^+ molecules was detected. Polar diatomics can attain 2.7 K in the diffuse medium. The cause of the ETR phenomenon has been interpreted as due to the radiative excitation of rotational levels by light from a

nearby infrared star. The modelling of the DIB profiles has led to the conclusion that the molecules responsible for DIBs showing ETR are polar while the others are non-polar.²⁵ In addition, rotational fits to the 5797.1 DIB, and consideration of the photo-dissociation rate for smaller species, indicate that its carrier is a molecule containing 5–9 heavy atoms.²⁶ But for the evident species, like C_6 , C_6H , HC_4CN^+ with absorptions in the visible, the electronic spectra in the gas phase have been obtained and compared with DIB data,¹⁶ leading merely to upper limits of their column density $<10^{11}-10^{12}\text{ cm}^{-2}$ in the diffuse clouds.

By serendipity, while studying the absorption spectra of organic radicals in neon matrices, invoked as intermediates in combustion and chemical reactions, it was noted that some of the cationic species possess not only transitions in the visible region but also the large $f > 10^{-1}$ oscillator strengths required to be candidates for the stronger DIBs (equivalent width (EW) $> 50\text{ m}\text{\AA}$), even with column densities of around 10^{12} cm^{-2} . One such example was the investigation of $\text{C}_7\text{H}_3/\text{C}_7\text{H}_3^+$ isomers: the protonated cumulene $\text{H}_2\text{C}_7\text{H}^+$ has a transition with a dominant origin band near 408 nm with $f \approx 0.2$.²⁸ An appealing fact is that the isoelectronic neutral cumulenes H_2C_n with $n = 3-5$ are known constituents of dense interstellar clouds.²⁹

It proved possible to record the electronic transition of $\text{H}_2\text{C}_7\text{H}^+$ in the gas phase using an ion trap.³⁰ Unfortunately a DIB at the wavelength of its origin band, 427 nm, is obscured by a He line. It is also a matter of debate³¹ whether small cations should be considered because electron recombination may limit their concentration. Nevertheless, these spectroscopic studies have shown that carbon chain like molecules, though not linear, are candidates for the structured DIBs considered by Oka. As an addition to this, the electronic spectra of the organic radicals, C_9H_9 , C_9H_5 obtained by the resonant multiphoton ionization technique following their production in a pulsed discharge source, show absorptions some of which coincide with weak DIBs,³² though this may be accidental and will be difficult to prove. A list of the species not detected in diffuse clouds including upper limits on their column densities can be found in a review article.³³

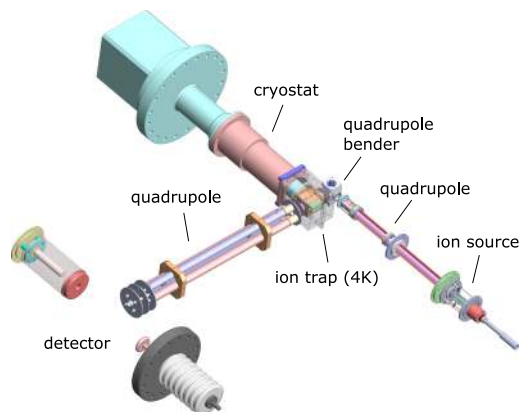


FIG. 3. A schematic of the ion trap apparatus used to record the gas phase electronic spectra of cold molecular ions. Ions produced by electron impact are mass-selected and injected into a radiofrequency trap (22-pole or 4-pole) where the internal degrees of freedom are relaxed via collisions with 4 K helium buffer gas. In the trap they interact with laser radiation after which the contents are extracted and analyzed using a mass-spectrometer.

B. Polycyclic aromatic hydrocarbons

In the 1970s, a set of emission bands in the infrared region (UIBs) were discovered^{34,35} and have since been observed in many astrophysical environments (see Ref. 36). It was recognised that these features appear at wavelengths consistent with the vibrational modes of aromatic molecules.³⁷ As a class the polycyclic aromatic hydrocarbons (PAHs) satisfy the criteria required to explain these emission bands. The PAH hypothesis is known since the 1980s^{38,39} and on this basis they are proposed to account for 10% or more of the cosmic carbon budget. Unfortunately it is not possible to identify individual molecules because the observed infrared emission bands are so broad, 10 cm^{-1} , and indistinct. Neutral and ionized PAHs and protonated derivatives have also been often proposed as candidates for the DIBs.⁴⁰

Parallel to the study of carbon chains, numerous electronic spectra of polycyclic aromatic hydrocarbon ions (PAH^+) were measured in argon and neon matrices⁴¹ and just a handful in the

gas phase by a cavity ring-down technique.⁴² Recently, mass-selected PAH⁺ cations have been stored in an ion trap where collisional cooling has enabled the electronic spectra of species as large as protonated coronene C₂₄H₁₃⁺ to be observed at temperatures of 10–30 K.⁴³ Though most of these ions, open-shell PAH⁺ and some protonated ones H.PAH⁺, possess electronic transitions in the DIB region, none could be identified as DIB carriers. However, as is the case of the carbon chains, many of the electronic transitions have *f* values around 10⁻², and thus though these species may well be present in the diffuse clouds, their column densities are smaller than 10¹¹–10¹² cm⁻². Subsequently the argument was made that such systems would have to be large with 50 or more carbon atoms to be photostable in the diffuse medium.^{44,45}

One major reason for using a rf trap is to relax the internal degrees of freedom by collisions with cryogenically cooled helium to temperatures characteristic of the internal medium: 2.7 K to say 60 K. In the diffuse clouds, the dominant mechanism for achieving this in large systems is through the emission of infrared radiation. In the trap a stored ion collides about every microsecond with cold helium and thus in due course both the vibrational and rotational degrees of freedom are equilibrated to a low temperature. In the case of the medium size PAH⁺ systems studied, e.g., protonated pyrene or coronene, temperatures 15–20 K were experimentally chosen.⁴³ The comparison of the laboratory spectra and DIBs was negative leading us to conclude that even PAH⁺ ions containing around 50 atoms can be excluded as DIB carriers.

C. Fullerenes

The fullerenes were first discovered in experiments that were carried out with the aim of understanding the mechanism of formation of carbon chains in circumstellar and interstellar environments.⁴⁶ It was immediately recognised that this newly identified allotrope of carbon could play a role in the DIB puzzle. Furthermore, derivatives of these carbon structures containing cosmically abundant species have long been proposed as candidates to explain several astronomical phenomena.⁴⁷

After Krätschmer *et al.* synthesised C₆₀ in macroscopic amounts,⁴⁸ spectroscopic studies of the electronic transitions of neutral and ionized C₆₀ and C₇₀ were made.^{49–53} Although neutral C₆₀ has only weak absorption bands in the region of interest for the DIBs, the electronic spectrum of the positive ion C₆₀⁺ recorded in a 5 K neon matrix revealed two prominent absorption features in the near infrared.⁵² As early as 1987, Kroto highlighted its astronomical importance⁵⁴ by writing “The present observations indicate that C₆₀ might survive in the general interstellar medium (probably as the C₆₀⁺ ion) protected by its unique ability to survive processes so drastic that, most if not all, other known molecules are destroyed.”

In 1993 when the C₆₀⁺ neon matrix spectrum was recorded,⁵² a prediction of the gas-phase absorption wavelengths was made: “Thus the origin of the C₆₀⁺ 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.” A year later, two DIBs were detected within this expected wavelength range and proposed to be caused by C₆₀⁺ in diffuse clouds.⁵⁵ Several later studies

were able to confirm the interstellar nature of these absorption bands, improve the signal to noise ratio, and detect these DIBs along a number of lines of sight.^{56–58} In common with all matrix spectra the wavelengths of the C₆₀⁺ absorptions are perturbed from the free gas phase values due to the interaction with the host rare gas atoms. Such solid state effects also lead to a broadening of the spectral features. A consequence of this is that a gas phase spectrum of C₆₀⁺ was called for in order to make an unambiguous comparison with the astronomical observations.^{59,60}

A major reason to develop the ion trap approach utilising collisional cooling to achieve astrochemically relevant temperatures was to resolve this outstanding problem from the 1990s and obtain the electronic spectrum of C₆₀⁺ under conditions similar to the diffuse clouds. To recall, polar diatomics including CH⁺, CH, and CN were detected in the interstellar medium already in the 1930s and 1940s and provided an early indication of low interstellar temperatures (see Ref. 33). This was later recognized as the cosmic microwave radiation blackbody temperature. Non-polar species, C₂ and C₃, identified by their electronic transitions have higher rotational temperatures, say 40–60 K, as does H₃⁺ studied extensively by infrared absorption.⁶¹ The large number of degrees of freedom of C₆₀ makes cooling in supersonic expansions difficult and such problems have been described.⁶² In 2015, experiments on C₆₀⁺ in the ion trap proved to be successful and for the first time a molecular carrier for some of the DIBs could be identified.

IV. GAS PHASE C₆₀⁺: FIRST IDENTIFICATION OF A DIB CARRIER

A. Approach

The obstacle to overcome the recording of the gas phase C₆₀⁺ spectrum was the lack of a suitable approach to detect a signature of the absorption process. Direct spectroscopy by monitoring the attenuation of light in a standard Beer-Lambert experiment, $I = I_0 \exp(-\sigma nl)$, is not feasible due to the small column densities of ions in the trap. For example, the attenuation of light $(1 - I/I_0)$ due to absorption at 9577 Å by C₆₀⁺ ions with a column density of 10⁴ cm⁻² is just 5×10^{-11} .⁶³ It is interesting to contrast this with the situation prevailing in the diffuse clouds: with their parsec dimensions and a molecule column density of 10¹³ cm⁻² the observed attenuation of starlight at 9577 Å is 9%.

Ion counting approaches offer unique sensitivity for spectroscopy. Rather than monitoring the attenuation of light, such methods typically detect a change in the number of ions that occurs following the resonant excitation of the transition of interest. This allows spectra to be obtained even when the column density of ions in the trap is low. In one action spectroscopy method, a first laser photon is tuned to the transition of interest after which the ion cloud is exposed to higher energy radiation that induces the fragmentation of the molecular ion of interest. By monitoring the fragmentation yield as a function of the wavelength of the first laser, the spectroscopic signature can be detected. However, the use of action spectroscopy for a species such as C₆₀⁺ is also unfavourable. Although the lowest thermodynamic dissociation channel is the loss of C₂

and requires 7 eV, not far above this energetic threshold, the slow rate of fragmentation hinders this approach. Only with >20 eV excess energy does one observe a fragmentation rate in the ms range. This can be rationalized by statistical theories. A vacuum ultraviolet (VUV) laser would be required in a $1 + 1'$ action spectroscopy scheme, with the added drawback that the further one is from the energetic threshold, the poorer the Franck-Condon factors become for the transition to the continuum. Thus alternative methods to detect the absorption of a photon were sought.

One novel approach was demonstrated by the measurement of the electronic spectrum of N_2^+ . This relies on observing a change in the number of N_2^+-He complexes synthesised in the low temperature trap by the ternary association $N_2^+ + 2He \rightarrow N_2^+ - He + He$ after the electronic excitation of the cold N_2^+ ions.⁶⁴ The technique is general and has subsequently been used to detect the infrared spectra of ions⁶⁵ and requires the use of low (5 K) temperatures and high helium number densities (10^{15} – 10^{16} cm⁻³) in order to form weakly bound complexes in the rf trap. Experiments with C_{60}^+ have shown that at 6 K a few % can be converted to C_{60}^+-He , but at 4 K a conversion efficiency of more than 50% is reached. The steep temperature dependence on the number of C_{60}^+-He complexes is not yet understood and there may be another mechanism in addition to ternary association that occurs at the lowest cryogenic temperatures.

Whereas in the case of N_2^+ , the determination of the frequencies of individual rotation lines in the spectrum proved that the spectrum observed is of N_2^+ , and not that of N_2^+-He , in the case of large ions such as C_{60}^+ the unresolved rotational profile will overlap with that of C_{60}^+-He . Thus an alternative method that is experimentally easier to implement was adopted. This also requires as an initial step the formation of C_{60}^+-He but following resonant absorption of the laser photon, C_{60}^+ ions are produced. The electronic spectrum of C_{60}^+-He is thus measured rather than of the bare C_{60}^+ . The spectroscopic shift due to helium can be quantitatively evaluated by following the trend on the attachment of more helium atoms, $C_{60}^+-He_n$ ($n = 1-3$). This is expected to be small, as earlier studies show. Starting in 1989, a few electronic spectra of ionic complexes with helium were recorded at temperatures around 30 K.⁶⁶ The first measurements on N_2^+-He showed that these transitions are shifted by less than 1 Å in wavelength relative to N_2^+ . The exact shift could not be established because of the laser bandwidth.⁶⁷

B. Spectroscopic results

The C_{60}^+-He photodissociation spectrum recorded, this was at first in a 22-pole rf trap, showed the two strong features as in the neon matrix and at wavelengths within the uncertainty of the astronomical data on the 9577 and 9632 DIBs.⁶⁸ The 2.5 Å FWHM of the two laboratory bands is rather similar to the DIBs and the relative intensities of the bands are comparable to the EW ratio. Thus it was instantly apparent that the C_{60}^+-He spectrum is essentially that of C_{60}^+ , for astronomical purposes anyway, and confirmed the proposition⁵⁵ that the 9632 and 9577 DIBs are indeed of C_{60}^+ .

Following the identification of C_{60}^+ in diffuse interstellar clouds, several laboratory and astronomical aspects were elucidated. First of all, a larger part of the C_{60}^+-He spectrum was recorded.⁶³ Apart from the 9632 Å origin and the energetically close lying 9577 Å dominant bands, three absorptions lying at shorter wavelengths, and corresponding to vibrational excitation in the upper electronic state(s), are sufficiently intense that their detection in diffuse clouds could be attempted. At higher energies still the spectrum is complex due to vibronic and Jahn-Teller effects and awaits a theoretical analysis but because the C_{60}^+ molecule is rigid, the distortion is expected to be small. Nevertheless, the lowest energy structure in the ground electronic state is no longer icosahedral as for C_{60} . Theoretical calculations, though not at a high level, indicate that D_{5d} symmetry is the lowest though the D_{3d} minimum lies close by.⁶⁹ In D_{5d} symmetry the 9632 Å band is the origin band of the ${}^2E_{1g} \leftarrow X {}^2A_{1u}$ electronic transition of C_{60}^+ . The assignment of the 9577 Å band lying just 60 cm⁻¹ to higher energy to another excited electronic state could be made after experiments in the ion trap. This could be shown because the irradiation of the stored C_{60}^+-He at either 9577 Å or 9632 Å led to a complete attenuation of the number of complexes, indicating that both transitions arise from a common lower level. The electronic spectrum of C_{60}^+-He , spanning the wavelength range 9060–9640 Å, is shown in Figure 4.

The spectroscopic shift induced by the helium atom was established by measuring the dissociation spectra of $C_{60}^+-He_n$ ($n = 1-3$). A linear shift of 0.7 Å is established allowing the prediction of the wavelength maxima of the first five most intense bands of C_{60}^+ .⁷⁰ The inspection of the DIB literature and a specific search towards different reddened stars identified three further DIBs in addition to those at 9632 Å and 9577 Å, though the intensity of these is close to current detection limits. In the line of sight toward the star HD 183143, chosen because the 9577 and 9632 DIBs are particularly strong, there is more than one interstellar cloud, as evidenced by the potassium I line components. Lorentzian profiles (lifetime broadening) of the laboratory absorption bands were fit to the interstellar features after taking into account the Doppler shifts of the two clouds.⁷¹ The agreement, as shown in Figure 5, is excellent, and identifies in the century old puzzle the first DIBs to a specific molecule, and proves that C_{60}^+ is present in the diffuse clouds.

The FWHM of the laboratory absorptions is around 2.5 Å. This exceeds the widths expected on the basis of rotational contour simulations. These were carried out for C_{60} ,⁷² but a similar situation will prevail for C_{60}^+ , and indicate that at a low temperature of 6 K the unresolved profile should have a FWHM of around 1 Å. Thus the 2.5 Å width arises because of the internal conversion process, and the excited electronic state lifetime is around 2 ps according to Heisenberg's uncertainty relationship. The contour simulations show that only above 30 K would the rotational profile broaden to 3 Å. The FWHMs of the C_{60}^+ DIBs in the various measurements reported are all around 3 Å.

Attempts to detect the infrared emission bands of C_{60}^+ have been undertaken,⁷³ with suggestions that some of the stronger

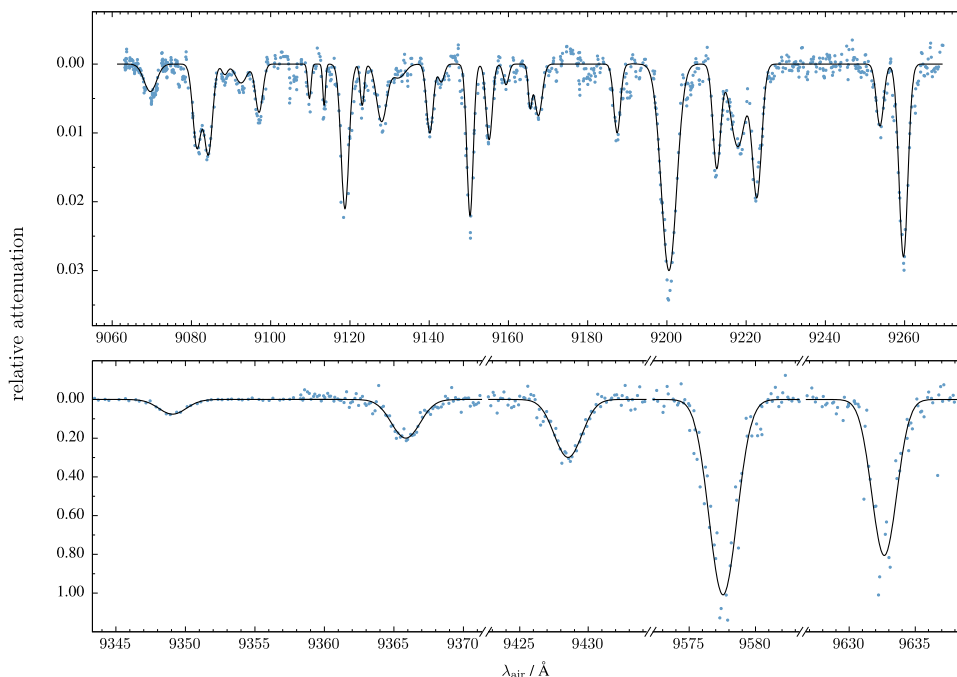


FIG. 4. The 6 K gas phase spectrum of C_{60}^+ –He recorded in the wavelength range from 9060 Å to 9640 Å. The spectrum is dominated by the two strong absorption bands near 9577 Å and 9632 Å. The intensities have been scaled by the relative absorption cross sections which are normalized to the strongest absorption. Reproduced with permission from E. K. Campbell *et al.*, *Astrophys. J.* **822**, 17 (2016). Copyright 2016 American Astronomical Society.

modes are observed. This will be difficult to prove; whereas the I_h symmetry of C_{60} dictates that only four modes are infrared active and these are the ones detected from various nebulae,⁷⁴ the lower D_{5d} symmetry of C_{60}^+ results in numerous allowed IR bands.

C. C_{60}^+ abundance in diffuse clouds

An important quantity in view of the identification of C_{60}^+ in diffuse clouds is its abundance. In astronomical measurements, this is described by the column density $N(C_{60}^+)$: the number of C_{60}^+ along the line of sight towards the reddened star in an area of 1 cm². It is evaluated according to $N(C_{60}^+) = \frac{mc^2}{\pi e^2} \frac{EW}{\lambda^2 f}$. In this formula, EW is the equivalent width of the DIB absorption and λ is the central wavelength. In the case of diatomic molecules, the oscillator strength f of the absorption is usually derived from lifetime measurements;

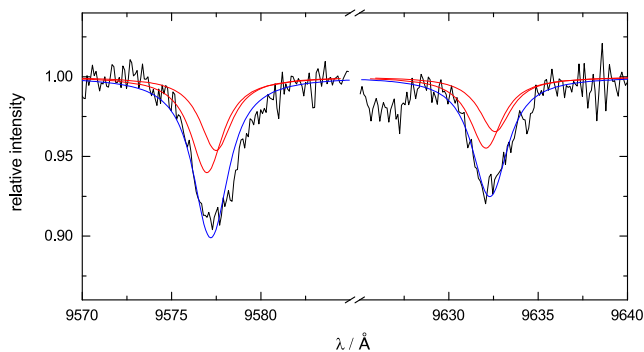


FIG. 5. Fits (blue) to the DIBs (black) observed toward HD 183143 that were originally reported by Foing and Ehrenfreund.⁵⁶ The region of the 9632 DIB has been corrected to take into account the Mg II stellar line contamination (see Ref. 71). Two Lorentzian profiles (red) have been fit to both DIBs. These have central wavelengths constrained by the extrapolated C_{60}^+ values and adjusted for the radial velocity of the two interstellar clouds. The plot shows the best fit to the astronomical data obtained by allowing the central wavelengths of the C_{60}^+ absorptions to vary by the reported experimental uncertainty of ± 0.2 Å.

for smaller polyatomics theoretical calculations are used. In the case of very large species such as C_{60}^+ , only low level methods are amenable. These yield $f \approx 0.05$ for the whole ${}^2E_{1g} \leftarrow X^2A_{1u}$ transition of C_{60}^+ ,^{69,75} which then has to be weighted with the Franck-Condon factors to obtain, for example, the value for the 9577 Å band. Estimates of this have also been made using the absorption intensities observed in a neon matrix, which requires knowledge of the ionic concentration, and yield a comparable f value.⁷⁶

Consequently we measured the cross section directly in the gas phase. In order to determine accurate absolute values of σ , a linear quadrupole ion trap was used.⁶³ In contrast to the 22-pole trap, in which the diameter of the stored ion cloud is typically larger than that of the laser beam, the effective potential of the 4-pole trap allows the former to be compressed, ensuring a good coaxial overlap between the two. The number of C_{60}^+ –He in the trap monitored as a function of the laser fluence, $N(\Phi)$, follows the exponential function $N(\Phi) = N_0 \exp(-\Phi/\Phi_0)$. Here the derived characteristic fluence Φ_0 provides information on the photo-fragmentation cross section, and under the experimental conditions used, in which the absorption of a photon always leads to dissociation, the absorption and fragmentation cross sections are identical. After taking into account the uncertainties of the experiment,⁶³ the cross sections at the wavelengths of the two strongest absorption bands were determined to be $\sigma(9577) = (5 \pm 2) \times 10^{-15}$ cm² and $\sigma(9632) = (4 \pm 2) \times 10^{-15}$ cm². These absolute values could then be used to directly calculate the column density of C_{60}^+ in diffuse clouds as the latter is given by $N(C_{60}^+) = \ln(I_0/I)/\sigma$. Astronomical measurements towards the reddened star HD 183143⁷⁷ give an intensity ratio I/I_0 of 0.91 at 9577 Å, implying $N(C_{60}^+) = 2 \times 10^{13}$ cm⁻². This is a substantial amount of carbon; for comparison $N(CH^+)$ or $N(CH)$ is around 10^{13} cm⁻² towards this star and $N(H_3^+) = 10^{14}$ cm⁻².⁶¹ As the column densities of small species in these environments rapidly

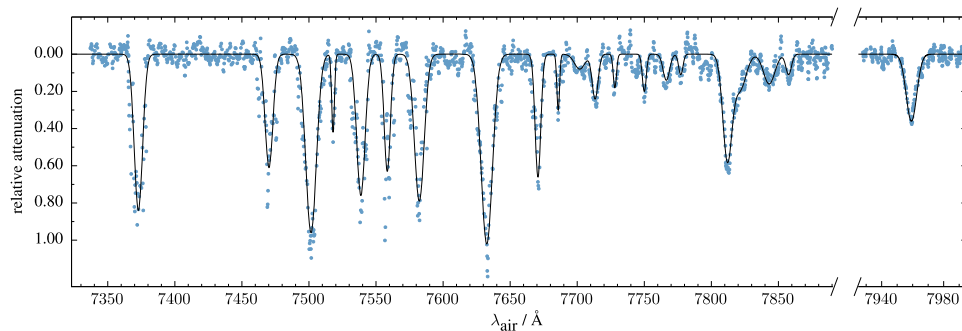


FIG. 6. Gas phase spectrum of C_{70}^+ –He below 10 K showing the lowest energy electronic transition, assigned as ${}^2E'_1 \leftarrow X{}^2E''_1$ in D_{5h} symmetry. Reproduced with permission from E. K. Campbell *et al.*, *Astrophys. J.* **822**, 17 (2016). Copyright 2016 American Astronomical Society.

decrease with increasing molecular size, the large $N(C_{60}^+)$ has important implications for the mechanisms that set the organic inventory.

In 2010 a major discovery was made: the identification of C_{60} in a young planetary nebula by its four characteristic infrared emission bands.⁷⁴ Subsequently these have been observed in a number of other nebulae.⁷⁸ On the other hand, the attempts to detect C_{60} in the diffuse clouds via its electronic spectrum have been unsuccessful.⁷⁹ The gas phase spectrum of C_{60} was recorded in 1991 by a resonant multiphoton ionization method in a supersonic beam,⁵⁰ later in helium droplets, and extensively in neon matrices.⁸⁰ C_{60} has a number of absorptions in the 6000 Å region, some of which have oscillator strengths comparable to C_{60}^+ (9632 Å) according to theory, and strong absorptions below 4000 Å though these are broad (100 Å) and thus difficult to detect as DIBs. An upper limit of $N(C_{60}) < 10^{11} \text{ cm}^{-2}$ has been inferred.⁷⁹ Taking this value in conjunction with $N(C_{60}^+) = 2 \times 10^{13} \text{ cm}^{-2}$, implies that around 98% of C_{60} becomes ionized on passing from the planetary nebula environments into the diffuse clouds.

These findings lead to fascinating questions and speculations. Of importance is just how C_{60} and C_{60}^+ are produced in the two regions. It has been suggested that both can be formed in a top down process through the photo-irradiation of PAH like species.⁸¹ Another question is whether or not C_{60}^+ is produced by the ionization of C_{60} expelled from the nebula of the dying carbon stars and collected in diffuse clouds. Furthermore, as diffuse clouds are precursors of dense clouds, where a rich variety of carbon chain like molecules (e.g., cyano-polyacetylenes) have been detected, one can speculate on the role played by the destruction of C_{60}^+ and related fullerenes containing N or O by high energy radiation in producing such species in dense clouds.

D. Other fullerenes and derivatives

To make progress on the question of the role played by other fullerene cations in the diffuse clouds, the electronic spectrum of C_{70}^+ –He was obtained.⁶³ The important difference from the C_{60}^+ –He spectrum is that rather than being dominated by two strong absorptions, the intensity is spread-out over around 20 features of comparable strength, with the origin band at 7959 Å being relatively weak. The spectrum is shown in Figure 6. Laboratory measurements show that the cross section at 7959 Å is three orders of magnitude smaller than that for C_{60}^+ at 9577 Å, implying that the C_{70}^+ absorptions as DIBs are not detectable. They would possess EWs of less

than mÅ, assuming an equal C_{60}^+/C_{70}^+ abundance in the diffuse clouds, and unfortunately this means that useful upper limits on the C_{70}^+ column density cannot be placed.

A similar constraint appears to be the case for the detection of another larger fullerene cation; attempts to record the spectrum of C_{84}^+ –He lead to a broad, unstructured, absorption precluding an appropriate spectroscopic signature for its detection among the DIBs. In addition, the presence of isomers among the larger fullerenes may result in spectral congestion. This argument also applies to the hydrogenated derivatives $C_{60}H_n^+$, obvious candidates in view of C_{60}^+ identification and the 90% cosmic abundance of hydrogen. The spectrum of $C_{60}H^+$ has been measured in the solution⁸² but is broad and thus unlikely to be responsible for the much narrower DIBs. Addition of further hydrogens will result in a large number of isomers and perhaps indistinct broad absorptions. However only future measurements in the laboratory can decide if such fullerene derivatives, as well as those containing N and O, can have a distinct spectroscopic signature as C_{60}^+ has. This also applies to doubly charged cations, C_{60}^{++} being the prominent example. Recently it could be shown that C_{70}^{++} has a suitable absorption but C_{60}^{++} does not.⁸³ As the ionization potential of C_{60}^+ is below the 13.6 eV energetic threshold for interstellar photons, C_{60}^{++} is expected to be present in diffuse clouds; however, the lack of a suitable spectral signature in the visible will preclude its detection. The absorption of C_{70}^{++} around 700 nm has a large cross section but the width of the band profile would result in a shallow interstellar feature making astronomical detection difficult. The absorption spectra of smaller fullerene cations produced top-down, e.g., from the fragmentation of C_{60}^+ , await laboratory investigation.

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