Astron. Astrophys. 319, L59–L62 (1997)

ASTRONOMY AND ASTROPHYSICS

LETTER

Letter to the Editor

New evidences for interstellar $C_{60}^{+\star}$

B.H. Foing[1,2] **and P. Ehrenfreund**[3,2]

[1] Solar System Division, ESA Space Science Department, ESTEC/SO, 2200 AG Noordwijk, The Netherlands
[2] Institut Astrophysique Spatiale, CNRS, Bat 121, Campus d'Orsay, France
[3] Leiden Observatory, P.O. Box 9513, 2300 RA Leiden, The Netherlands

Received 22 October 1996 /Accepted 21 November 1996

Abstract. The discovery and synthesis of fullerenes led to the hypothesis that they may be present and stable in interstellar space. As first evidence for the largest molecule ever detected in space, we have recently detected two new diffuse interstellar bands (DIBs) in the near-infrared that are consistent with laboratory measurements of the C_{60} cation. The inferred abundance (up to 0.9 % of cosmic carbon locked in C_{60}^+) suggested that fullerenes may play an important role in interstellar chemistry. We present new observations towards HD183143, HD37022 and HD 80077 at 9600 Å from CFHT and ESO. The high quality of the spectra confirms without doubt the presence of the two DIBs at 9577 and 9632 Å and allows to measure reliably their strength, width and band ratio. The two correlated DIBs decrease in a UV shielded cold cloud (HD80077) but increase in a region dominated by extreme UV radiation (HD37022), with a band ratio constant within errors. Both DIBs show the same width, also consistent with a common carrier. This width of 3 cm^{-1} is compatible with rotational contours of C_{60} fullerene molecules. These results bring new evidences for C_{60}^+ in addition to the match with laboratory spectra.

Key words: ISM:molecules; ISM:dust; ISM:individual: HD183143, HD37022, HD80077; Line:profiles

1. Introduction

C_{60} was synthesized and its polyhedral geometry was discussed for the first time by Kroto et al. (1985), which led to the Nobel prize for Chemistry in 1996 for Kroto, Curl and Smalley. A few years later C_{60} was produced in macroscopic quantities by vaporizing graphite in a He atmosphere (Kraetschmer et al. 1990).

On Earth, fullerenes C_{60} and C_{70} have been identified by laser desorption and other techniques in shock produced brecchias of the Sudbury impact structure in Ontario (Becker et al. 1994). In space, fullerenes have been detected in an impact crater on the LDEF spacecraft and in meteorites (di Brozzolo et al. 1994, see also Ehrenfreund & Foing 1996b for a review, thereafter EFb). It has been discussed that the inhibition of the fullerene growth mechanisms by hydrogen will limit the formation of C_{60} to hydrogen depleted environments in space (Goeres & Sedlmayr 1992). However, Gerhardt et al. (1987) showed that fullerenes form also in significant quantities in the presence of H and O. The spontaneous formation and stability of fullerene compounds have suggested their existence in the interstellar medium in relation to carbon dust (Kroto & Jura 1992). Two main sources for the formation of astrophysical fullerenes are considered (see EFb): (i) in the outflows of mass losing stars, graphite-like material can be processed by shocks or cosmic rays to produce fullerenes or (ii) interstellar processes, such as the build-up of C_2-C_{10} chains from C^+ insertion, ion-molecule and particularly neutral-neutral reactions (Bettens & Herbst 1996). Long chains can subsequently form polycyclic rings which can isomerize as small fullerenes above C_{35}. Larger fullerenes can grow from further C addition with particular accumulation at the most stable fullerene C_{60}. Interstellar hydrogenated fulleranes have been extensively discussed by Webster (1995). C_{60}^+H was proposed to be likely the most abundant fullerene analogue in space (Kroto & Jura 1992). Endo-and exohedral fullerenes associated with metals (Mg, Al, Si) may be also present in abundance in circumstellar and interstellar environments.

2. Diffuse interstellar bands and fullerenes

The long-standing problem of the identification of the Diffuse Interstellar Band (DIB) carriers has seen spectacular progress in the recent years (see Herbig 1995 for a review). The current number of $\sim$ 150 DIBs implies that the carriers may be classes of molecules which reside ubiquitous in the interstellar medium. Recent observations indicate that DIBs originate in large carbonaceous gas phase species (see Herbig 1995 for a review). The possible carriers which are mainly discussed are C-chains,

Send offprint requests to: B.H. Foing

$\star$ Based on observations with CFHT 3.6m and ESO CAT telescopes.

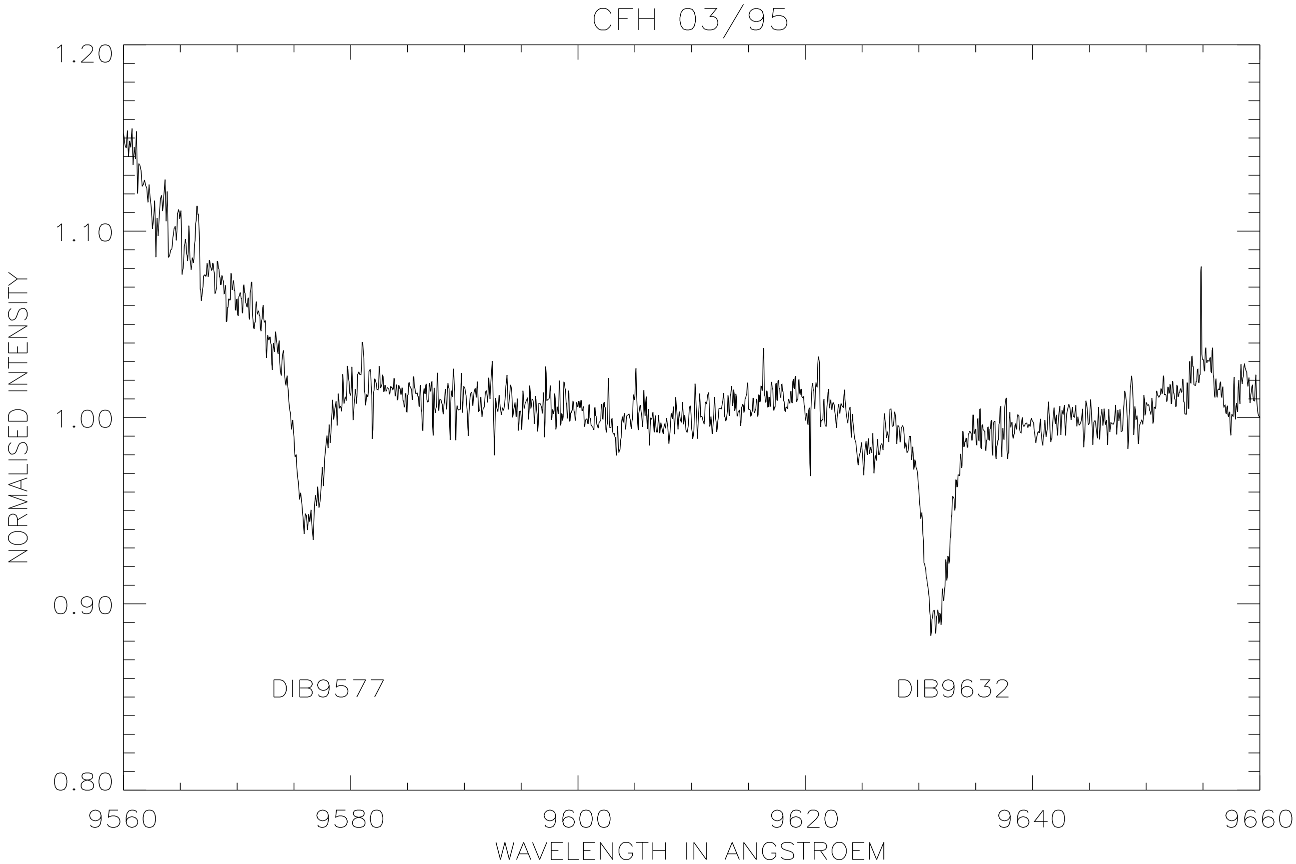

Fig. 1. Telluric corrected spectrum of HD183143 (Spectral type B7Iae) observed under very dry conditions at CFHT (less than 0.25 mm precipitable water or 10 times better than for original interstellar C_{60}^+ discovery at OHP). The star spectrum has been divided after instrumental corrections by a spectrum of a reference star of similar spectral type. This allowed to divide the stellar lines and limit flat field variations. Residuals from telluric water lines are almost absent. The two DIBs at 9577 and 9632 Å are confirmed with the same width of 2.85 Å consistent with the C_{60}^+ assignment and expected rotational contour broadening with temperature 60 ± 10 K.

polycyclic aromatic hydrocarbons (PAHs) and fullerenes. A recent survey for band correlations in single clouds reveals ionization and destruction properties for the DIB carriers which are strongly dependent on the local UV radiation field (Cami et al. 1996). Recent detections of substructures in the profile of the DIBs at 5797, 6379 and 6613 Å indicate - in comparison with model calculations of PAHs and fullerenes - that the responsible molecular carriers would correspond to large PAHs with more than 40 C atoms, chains of $\sim$ 12-18 C atoms, 30 C rings or fullerenes (Ehrenfreund & Foing 1996a). The 6613 Å DIB profile shows a three-peak structure with a separation of 1.5 cm^{-1} consistent with C_{60} fullerene rotational contour calculations. Assuming a spherical symmetry the rotational constant is defined as 0.0028 cm^{-1} which is very similar to the value derived for C_{60}.

Whereas fullerenes decompose in condensed media in the presence of oxygen and light, isolated fullerenes are stable even in intense radiation fields and could be at the origin of several diffuse interstellar bands (Kroto & Jura 1992). The polyhedral carbon ion C_{60}^+ was proposed by Kroto et al. (1987) and Léger et al. (1988) to be an excellent possible DIB carrier. C_{60} is expected to be the most stable and dominant fullerene during carbon clustering. The low ionization potential of C_{60} (7.61 eV) will favour its ionization in the diffuse medium outside dark clouds. However, measured laboratory spectra of C_{60} and C_{60}^+ do not show any strong bands in the visible.

We searched for C_{60}^+ in the diffuse medium in the near-infrared and found recently two diffuse bands satisfying the classical criteria for DIBs at 9577 Å and 9632 Å that are coincident within 0.1 % with laboratory measurements of C_{60}^+ in a neon matrix (Foing & Ehrenfreund 1994). To ensure a consistent identification, several criteria of the specific candidate C_{60}^+ were investigated and we discussed why the derived Ne matrix shift of $\sim$ 10 cm^{-1} is expected for a near-infrared transition from the deep C_{60}^+ fundamental level (Foing & Ehrenfreund 1994, Ehrenfreund & Foing 1995). We present in this letter new high quality spectroscopic data giving further evidences for the existence of C_{60}^+ in space.

3. New observational results

Observations were obtained at the 3.6 m CFHT (Coude f/8 spectrometer, March 1995) and ESO 1.5 m CAT (Coude Echelle Spectrometer CES, November 1994) telescopes. The spectral resolving power was 50.000 and the S/N in excess of 500, in areas free of telluric lines. Observations in the range of 9600 Å are very difficult to achieve because of the strong telluric absorptions. Observations under exceptionally dry conditions at CFHT (less than 0.25 mm precipitable water) and dry conditions at ESO made it possible to obtain high quality spectra of the DIBs at 9577 and 9532 Å, previously detected at OHP in 7 stars. Also the reduced water absorption and instrument efficiency allowed to limit time between exposures of reddened stars and telluric standard stars, further improving the final correction. Fig. 1 shows the telluric corrected spectrum of HD183143 measured at CFHT in March 1995 in the near-infrared. The spectrum confirms without doubt the existence and position of the DIBs at 9577 and 9632 Å. The equivalent width of the bands was measured in 10 Å windows and is listed in Table 1. The 9632 Å DIB is slightly blended by a He I line (at 9625.6 Å), but due to the high resolution the bands could be well separated. The defined ratio of the two bands of 1.17 ± 0.2 in this line of sight is more reliable than any other previous measurements that included telluric and stellar residuals. The wavelength difference between the two lines is 55.2 ± 0.2 Å (or 60 cm^{-1}). We measure the same width of 2.85 ± 0.2 Å for both bands and a possible slight far wing contribution in a 15 Å window.

We studied these two near-infrared DIBs towards other lines of sight in different environments, to probe the ionization properties of the carrier molecule. Fig. 2 shows CAT/CES spectra toward the Orion Trapezium star HD37022 and toward HD80077, a star located behind a translucent molecular cloud. After telluric correction the S/N is 350, but decreases to 150 for the cores of telluric lines stronger than 50 % (as seen in Fig. 2). Residuals at 9580 and at 9637 Å affect partly the red wings of both DIB profiles, but do not affect strongly their measured equivalent width and band width. Spectroscopic measurements are listed in Table 1. An enhanced red-wing asymmetry in the spectrum of HD37022 can be observed.

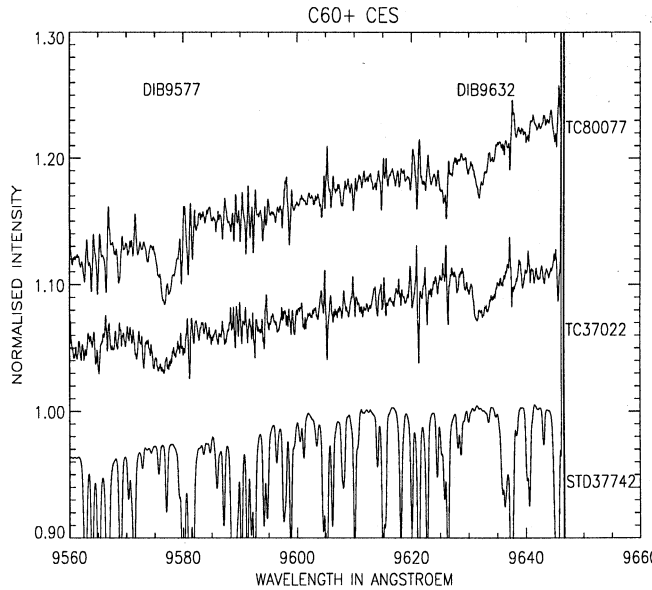

Fig. 2. Telluric corrected (TC) near-infrared spectra of HD37022 and HD80077 obtained with the CAT/CES telescope. Outside the telluric cores the S/N of those spectra is more than 300 and both DIBs at 9577 and 9632 Å are clearly detected. The width of the bands in HD37022 is broader than toward HD 80077 consistent with a C_{60}^{+} contour rotational broadening with temperature 130 ± 30 K. An uncorrected spectrum of the standard HD37742 displays (reduced by 4!) the water absorption under the moderately dry conditions at ESO.

Table 1. Spectroscopic parameters of the two near infrared DIBs attributed to C_{60}^{+}, measured in our program stars: normalized Equivalent Width per reddening (in mÅ), Full Width at Half Maximum (FWHM) and band ratio (9632/9577 Å) with estimated $\pm$ 2 σ errors.

Star	E_{B-V}	9577 (mÅ)	9632 (mÅ)	FWHM Å	Band ratio
HD183143	1.28	208	243	2.85±0.2	1.17 ±0.2
HD37022	0.35	330	360	4.00±0.3	1.09 ±0.3
HD80077	1.52	92	79	2.90±0.4	0.86 ±0.3

4. Environmental variations of DIB strength

These new high quality observations confirm the existence of the two DIBs discovered at OHP in 1994 (Foing & Ehrenfreund 1994). The separation of 60 cm^{-1} is found constant for different lines-of-sight irrespective of stellar or interstellar velocities. It is an important finding that the normalized strength of the total equivalent width of these two DIBs toward HD 37022 (690 mÅ/E_{B-V}) is higher than toward the diffuse ISM reference star HD183143 (451 mÅ/E_{B-V}). A value of only 171 mÅ/E_{B-V} is measured toward HD80077. This indicates a strong dependence of the DIB carrier on the local UV radiation field and argues for an ionized molecule, which is not significantly secondly ionized or destroyed by hard UV radiation. In this context we note the measured ionisation potential of 7.6 eV for C_{60} and of 11.3 eV for C_{60}^{+}, respectively. C_{60}^{++} can revert naturally to C_{60}^{+}, while many double ionized species (such as PAHs $<$ 50 C atoms) have a high probability of being dissociated, leading to low abundances (Allain et al. 1996).

We have recently measured the complete DIB spectrum towards HD37022 (Spectral type O6) (Cami et al. 1996). This target, with E_{B-V} of 0.35 is located behind the HII region in Orion. Limits for hydrogen column densities for HD37022 are log N(HI) < 21.04 and log N(H_2) < 17.65 (Savage et al. 1977). Nearly all DIBs are very weak or absent toward this target, indicating the destruction of DIB carriers in the HII region in the line of sight. Notable exception are the DIBs at 6284 Å and 5780 Å, showing an equivalent width/E_{B-V} of 0.93 and 0.3 that of HD183143. The extreme UV stability of the 9577:9632 carrier molecule is even more remarkable: they are the only known DIBs to show an increased strength (per unit reddening) towards HD37022 compared to HD183143 (see Table 1) among measurements of 50 other strong DIBs (Cami et al. 1996).

HD80077 is a superluminous hypergiant (Spectral type B2Ia) and located in the field of Pismis 11. Density and temperature inferred from C_2 are n $\sim$ 250 cm^{-3} and T $\sim$ 25 K, respectively (van Dishoeck & Black 1989). The reduced strength of the two near-infrared DIBs seems to be related to the molecular cloud in the line of sight, which prevents the ionization of the carrier due to the reduction of the ambient UV field.

We had shown that the two DIBs are well correlated in seven stars (Foing & Ehrenfreund 1994), which we verify here. Even though the 9577 and 9632 Å DIBs show very large variations of total normalized strength of 0.45, 0.69 and 0.17 Å /E_{B-V} in very extreme environmental conditions, their band ratio is compatible with a single value (within errors). This is indicating a common or very similar carrier for the two DIBs.

5. DIB width and $C_{60}{}^{+}$ rotational contour

The measured band width is the combined result of the instrumental resolution, the velocity distribution of the line-of-sight interstellar clouds, and the rotational contour profiles. For the CFHT profile the instrumental resolution is 0.2 Å. The cloud velocity dispersion towards HD183143 lies between 10 and 20 km/s based on NaD line saturated absorption profiles. This can be translated to a 0.32-0.65 Å Doppler broadening at 9600 Å. Deconvolving the measured 2.85 Å width for these effects leads to an intrinsic FWHM of 2.75-2.80 Å for the contour profile, equivalent to 3.02 $\pm$ 0.05 cm^{-1}. This value is remarkably similar to rotational contour calculations of C_{60} fullerenes (Edwards & Leach 1993) for temperatures between 50 and 80 K.

The contour profile arises from the rotational population in the fundamental electronic level with distribution depending as $(2J+1)^2$. $e^{(-BJ(J+1)/kT)}$ for a spherical molecule, where B is the rotational constant and T the rotational temperature. Maximum population is obtained for $(2J_0 + 1)^2 = 4kT/B$ and half maximum population for 0.5 and 1.63 J_0. The P and R branches correspond to the frequency differences ΔEP= 2B(J+1) + ΔB (J+1)(J+2) and ΔER = -2BJ + ΔBJ(J-1), where ΔB is the difference of rotational constants. This leads to a branch peak separation of $4BJ_0 + 2B + 4\Delta BJ_0$, where the first term $4BJ_0$ dominates with C_{60} parameters and interstellar temperature. From the calculated contours of the C_{60} superposed P and R branches (Edwards & Leach 1993) for $|\Delta B| = 0 \rightarrow 2$ %, the calculated widths are 2.25 - 2.6 cm^{-1} at 50 K and 3.1 - 4.0 cm^{-1} at 100 K. The observed DIBs width for the HD183143 line-of-sight is thus consistent with a fullerene transition assignment for a reasonable range of temperature 60 $\pm$ 10 K. In addition the excess broadening of the DIBs toward HD37022 would be consistently explained by rotational temperatures of 130 $\pm$ 30 K, and a profile asymmetry also compatible with a limited ΔB/B distortion from fundamental to first excited level.

6. Conclusion

The presence of soot material in C-rich stars, the spontaneous formation and the remarkable stability of the fullerene cage suggests the presence of fullerene compounds in interstellar space. Fullerenes may be present as neutral and ionized species in the diffuse interstellar medium and dominantly neutral in dense clouds. Our high quality measurements of the two DIBs at 9577 and 9632 Å in different interstellar regions indicate a rigid large ionized carrier molecule, surviving most efficiently in regions dominated by hard UV radiation. They are the only two known DIBs to be relatively enhanced in HD37022 (an extreme UV dominated region). The band ratio stays constant within 30% (2σ errors), even for a range of 400 % change in strength/E_{B-V}. The correlated strength and similar width of both DIBs suggest that they originate from the same carrier. The width (3.0 cm^{-1}) is compatible with rotational contours of a fullerene molecule (Edwards & Leach 1993). It is interesting to note that the assignment to such a sphere molecule based only on astronomical data could be extended to other fullerene compounds before detailed laboratory spectroscopy is available. These new observations bring further evidence to the identification of interstellar $C_{60}{}^{+}$.

We reiterate the need for laboratory measurements of $C_{60}{}^{+}$ gas phase absorption as well as reliable oscillator strengths for a definite identification of interstellar $C_{60}{}^{+}$. Besides the interest for the DIB problem, the detection of fullerenes in significant quantities opens a way for a fascinating interstellar catalytic chemistry.

References

Allain T., Leach S., Sedlmayr E., 1996, A&A 305, 616

Becker L. et al., 1994, Science 265, 642

Bettens R.P.A, Herbst E., 1996, ApJ, in press

Cami J., Sonnentrucker P., Ehrenfreund P., Foing B.H., 1996, submitted to A&A

di Brozzolo F.R., Bunch T.E., Fleming R.H., Macklin J., 1994, Nature 369, 37

Edwards S.E., Leach S., 1993, A&A 272, 533

Ehrenfreund P., Foing B.H., 1995, Planetary & Space Science 43, 10/11, 1183

Ehrenfreund P., Foing B.H., 1996a, A&A Lett. 307, L25

Ehrenfreund P., Foing B.H., "Fullerenes in space", 1996b, submitted to Advances in Space Research

Foing B.H., Ehrenfreund P., 1994, Nature 369, 296

Gerhardt P., Loffler S., Homann K.P., 1987, Chem. Phys. Lett. 137, 306

Goeres A., Sedlmayr E., 1992, A&A 265, 216

Herbig G.H., 1995, ARA&A 33, 19

Kraetschmer W., Lamb L., Fostiropoulos K., Huffman D.R., 1990, Nature 347, 354

Kroto H.W. et al. 1985, Nature 318, 162

Kroto H.W. 1987, Polycyclic Aromatic Hydrocarbons and Astrophysics, eds. Leger, A. and d'Hendecourt, L., Reidel Publishing Company, 197

Kroto H.W., Jura M., 1992, A&A 263, 275

Leger A., d'Hendecourt L., Verstraete L., Schmidt W., 1988, A&A 203, 415

Savage et al. 1977, ApJ 216, 216

van Dishoeck E.F., Black J.H., ApJ 340, 273

Webster A., 1995, in Proceedings:'Diffuse Interstellar Bands', eds. A. Tielens T. Snow, Kluwer, 349

This article was processed by the author using Springer-Verlag LaTeX A&A style file *L-AA* version 3.