Laboratory confirmation of C_{60}^{+} as carrier of two diffuse interstellar bands

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In 1994 two diffuse interstellar bands (DIBs) at 9632 and 9577 Å were detected and proposed by Foing & Ehrenfreund [1] to be the absorption features of C_{60}^{+}. This was based on the proximity of these wavelengths to the two prominent absorption bands of C_{60}^{+} measured in a neon matrix [2]. Subsequent astronomical measurements [3,4] provided evidence for the interstellar nature of the 9632 and 9577 Å bands, as well as their recent detection in protoplanetary nebulae [5]. Confirmation of the assignment required the gas phase spectrum of C_{60}^{+}, which has taken 20 years. The approach which has succeeded to obtain these data confines C_{60}^{+} ions in a 22-pole radiofrequency trap, cool them by collisions with high density helium allowing *in situ* synthesis of $C_{60}^{+}-\mathrm{He}$ at 5.8 K. The photofragmentation spectrum of the $C_{60}^{+}-\mathrm{He}$ complex is then recorded using a cw diode laser. In order to infer the position of the absorption features of the bare C_{60}^{+} ion, measurements on $C_{60}^{+}-\mathrm{He}_2$ were also made. These show that the presence of the additional helium atom shifts the absorptions by less than 0.2 Å, much less than the accuracy of the astronomical measurements. The two absorption features in the laboratory have band maxima at 9632.7(1) and 9577.5(1) Å, with FWHM of 2.2(2) and

2.5(2) Å at 5.8 K, comparable with the DIBs. Collective agreement of their positions, widths and relative intensities derived from our gas phase measurements leads to the first definite identification of two bands among the several hundred DIBs features known [6].

The DIBs are absorptions seen towards reddened stars and were recognized as such around a hundred years ago [7]. They possess different intensities (equivalent width, EW), band widths (FWHM ranging from 0.2 to several Å) and sometimes show asymmetry or even features typical of unresolved rotational profiles of polyatomic molecules. Though a number of hypotheses have been put forward as to the carriers [6], no definite identification could be made. Excluded from this list are the di- and triatomic species detected in diffuse interstellar clouds, e.g. CH^+, CN, C_2, C_3 and H_3^+. The presence of smaller polyatomic molecules is also indicated from microwave detections in similar environments , e.g. $c-C_3H_2$ [8]. Significant experimental progress came about in the last two decades because it became possible to measure in the gas phase at low temperatures $(10-80\,K)$ electronic spectra of carbon chains and ions [9] as well as of a few polycyclic aromatic cations with absorptions in the DIB range [6]. None of these unambiguously match the DIB absorptions.

Shortly after the discovery of C_{60} [10], the question of its relevance to the diffuse interstellar bands was raised [11]. It was soon apparent that neutral C_{60} did not have appropriate absorptions in the DIB range [12]. However it was pointed out by Jura and Kroto [13] that due to its low ionization potential (7.61 eV), in the diffuse interstellar clouds C_{60} would be present mainly as C_{60}^+ and hence a possible DIB carrier. In the latter work charge transfer complexes of $(C_{60}-M)^+$ were also considered and proposed as further candidates. With the discovery of C_{60} in planetary [14] and reflection nebula [15], interest in C_{60}^+ has reawakened.

In 1994 two DIBs were discovered at 9577 and 9632 Å [1]. Their proximity in wavelength to two absorptions bands of C_{60}^+ measured in a neon matrix [2] was pointed out and assignment to this cation proposed. The 9632 Å DIB would correspond to the origin band of the $^2\mathrm{E} - {}^2\mathrm{A}_u$ electronic transition in D_{5d} symmetry which is lower than the I_h symmetry of neutral C_{60}, because of a Jahn-Teller distortion as indicated by theoretical studies [16]. Further observations of the 9577 and 9632 Å DIBs followed, confirming their interstellar nature, though some variation in the relative EWs and minor differences in wavelengths were manifested [3,4,17]. The most recent has been the detection of these two absorptions in a protoplanetary nebula [5], where C_{60} itself has been identified by its IR vibrational transitions.

All the astronomical studies concluded that decision on the assignment has to await the gas-phase measurement of the C_{60}^+ absorptions at low temperatures. The criteria are well defined: band positions, widths and relative intensities [18]. Some doubt on this proposition was cast based on the lack of observation of two higher energy C_{60}^+ absorptions [2] in the interstellar medium [4]. In this letter, laboratory gas phase measurements are reported and shown to satisfy the aforementioned criteria. The results presented here prove that indeed the 9577 and 9632 Å DIBs are due to C_{60}^+.

In the past years we built an apparatus in order to measure the electronic spectra of cations of astrophysical interest at temperatures typical of the interstellar medium [19]. The central part of the instrument is a cryogenic $22-$pole radiofrequency trap [20] in which ions are confined and undergo collisions with cold, T = 5 K, and very dense, [He] $= 4 \times 10^{15}\,\mathrm{cm}^{-3}$, helium. In the case of smaller polyatomic cations we could show spectroscopically there are a sufficient number of collisions to ensure that the rotational and vibrational temperatures are equilibrated [21]. Under these conditions it became possible to synthesize *in situ* helium complexes of mass-selected ions *via* ternary association [22].

These experimental advances allowed us to obtain the electronic spectrum of $C_{60}^{+} - He$ by one photon excitation followed by the loss of the He atom. “Tagging” methods have been used for decades in spectroscopy of ions mainly in the IR [23] using rare gases, but also in the visible with helium attachment [24]. Due to the low binding energies of weakly bound complexes like $C_{60}^{+} - He$, temperatures below 8 K are required.

The measured spectra, presented in Figure 1, are in outstanding agreement with the two DIBs at 9632 and 9577 Å. As expected from the weak interaction of the helium, measurement of the corresponding absorption for $C_{60}^{+} - He_2$ (Extended Data Figure 1) indicates that the shift on the electronic transition is less than 0.2 Å.

The best fits to our data with a single function have been obtained using a Gaussian, rather than a Lorentzian. The band maxima are at 9632.7(1) and 9577.5(1) Å. The authors of ref [4] give 9632.6(2) and 9577.4(2) Å as the rest wavelength after careful correction for stellar lines. The extracted wavelengths towards different stars, given by refs. [3,4,17], are nearly all within 1 Å of those given above. Agreement with our laboratory data is remarkable; the systematic errors in the DIB measurements are larger. It should also be noted that several clouds are sampled along the line of sight.

Further support for the DIB assignment comes by comparison with the experimental FWHM. The values of the two interstellar bands are reported as 3.0(2) Å [4]. Our laboratory results lead to 2.2(2) and 2.5(2) Å at 9632.7(1) and 9577.5(1) Å, respectively. The FWHM of the C_{60}^+ rotational profile at 5.8 K is around 1 Å[25]. The lines are therefore broadened by internal conversion, indicating a lifetime of 2 ps in the excited electronic state. The somewhat larger FWHM of the DIBs is expected because of the higher rotational temperature in the diffuse clouds. Temperatures of non-polar molecules are higher than the 5.8 K in our measurements, for example H_3^+ [26] and C_3 [27] lie in the $30 - 80$ K range. FWHM values for the 9632 and 9577 Å bands recently detected in a protoplanetary nebula are reported as 2.0(3) and 2.3(3) Å [5], comparable to our gas phase data (Fig. 1).

The relative cross-sections of the 9632.7(1) and 9577.5(1) Å laboratory absorptions have been determined (Methods, Extended Data Figure 2) to be about equal, in accord with the EW of the DIBs. The latter vary somewhat in the published articles [3,4,17], and the 9632 Å DIB is partially blended with a MgII line, but the consensus appears to be that they are comparable or perhaps the EW of the 9577 Å DIB is a bit larger. In the study of the absorption spectrum in the matrix [2], it was not clear what these two transitions were due to. The current experiments clarify this: irradiation at either 9632.7 or 9577.5 Å leads to near complete attenuation in the number of complexes. This indicates that the two transitions arise from a single structural isomer. The implications are that both transitions originate from the $v'' = 0$ level of the D_{5d} structure ($^2A_{1u}$ for C_{60}^+ in D_{5d} symmetry) either to two excited electronic states separated by ca. 55 Å, suggested on basis of magnetic circular dichroism measurements in argon matrices, or to the two spin-orbit components of the upper state, ^2E_g in D_{5d} [28,29].

According to the absorption spectrum in the neon matrix [2], the next bands to higher energy are less than a factor of $4-5$ in intensity. A search for DIBs at 9366 and 9419 Å was reported in refs. [4] and [17]. In this region we have observed bands in the gas phase at 9365.9(1) and 9428.5(1) Å, as shown in Figure 1. From the result that a DIB at 9366 Å was not detected, the former study put an upper limit of 16 % of the 9577 Å band intensity. This is consistent with our measured relative cross-section of around 20 %. The other band was looked for in interstellar clouds at 9419 Å but not found. However, the absorption is at 9428.5(1) Å in the gas phase according to our measurement. In ref [4] both an 'unidentified' emission feature at 9429 Å and a 'depression' at 9428 Å are reported. Astronomical measurements in this region are difficult because of stellar lines.

Gas phase laboratory measurements at 5.8 K are in remarkable agreement with two DIBs proposed by Foing & Ehrenfreund [1] to be the result of absorption features of C_{60}^+. Our conclusion is based not only on wavelength but also on FWHM and relative intensity of these electronic transitions in the gas phase. This constitutes a breakthrough in the DIB mystery, lasting a century, providing the first unambiguous molecule identification.

Methods

The use of cryogenic traps for astrophysics and spectroscopy is well documented in the literature [20].

Experimental procedure C_{60}^+ was produced by 50 eV electron impact of the neutral gas at 10^{-4} mbar. After passing through a quadrupole mass filter, operated here in the transmission mode, the internally hot ions are turned through 90 degrees using an electrostatic quadrupole bender and injected into a 22-pole radiofrequency (amplitude, $V_0 = 160\,\mathrm{V}$, frequency, $f = 4.85\,\mathrm{MHz}$) ion trap. The use of the bender allowed separation of neutrals and ions. The trap is mounted onto the second stage of a closed cycle cryostat (Sumitomo, RDK-205E). Trapping is achieved by pulsing the potential of the entrance and exit electrodes and the trap contents are analysed using a quadrupole mass spectrometer and a Daly detector. Experiments are performed at a repetition rate of $1\,\mathrm{Hz}$.

The internal degrees of freedom of the ions are cooled *via* inelastic collisions with helium buffer gas which is in equilibrium with the temperature of the trap walls (nominal temperature, $T_{nom} = 5\,\mathrm{K}$). The $C_{60}^{+} - He$ ions are rotationally cold because the internal temperature of the ion is given by the mass weighted average of the translational temperature of the ions and the buffer gas,

$$T_{rot} = (m_1 T_2 + m_2 T_1)/(m_1 + m_2), \quad (1)$$

where m_1, T_1 and m_2, T_2 are the mass and translational temperature of the ions and buffer gas, respectively. For heavy $C_{60}^{+} - He$ stored in cold helium, a translational temperature of $150\,\mathrm{K}$ for the ions still leads to a rotational temperature $T_{rot} = 5.8\,\mathrm{K}$.

Around 10^5 C_{60}^{+} cm^{-3} per filling are loaded into the trap by lowering the potential of the entrance electrode for $200\,\mathrm{ms}$. Here they interact with high number density helium buffer gas, $[\mathrm{He}] = 4 \times 10^{15}\,\mathrm{cm}^{-3}$, for $500\,\mathrm{ms}$. The helium is introduced by resonantly exciting a piezo valve with $4.5\,\mathrm{V}$ in amplitude at a frequency of $3.8\,\mathrm{kHz}$. In the trap $C_{60}^{+} - He$ complexes are formed *via* ternary association. Due to extremely slow cooling of all vibrational modes to their ground states, attachment of He to primary ions is very inefficient. However, a few $\%$ are sufficient, especially because a large fraction can be fragmented. After pumping out the gas for 100 ms, the ion cloud is exposed to cw radiation produced from a homebuilt diode laser (up to 100 mW, ~ 12 MHz bandwidth), which is gated with a mechanical shutter and open for a period of 300 ms. To avoid power broadening, only 2 mW have been used for recording the two bands at 9632.7(1) and 9577.5(1) Å. For the other two 20 to 30 mW were required to obtain an attenuation of 20 %. The potential of the exit electrode is lowered and the contents extracted and analysed 150 ms after irradiation. The resulting laser induced attenuation of the number of complexes was monitored as a function of laser frequency yielding photofragmentation spectra.

Relative photoabsorption cross-sections In the present experiment a confined ensemble of some thousand $C_{60}^{+}-He$ complexes, $N(P)$, is exposed to a cw diode laser. As can be seen from Extended Data Figure 2, the effective power density in the trap (diameter of the ion cloud, 0.8 cm) can be varied over a wide range. The observed attenuation curves have been fit with the exponential function,

$$N(P) = N_0 \exp -(P/P_0). \tag{2}$$

The characteristic power, P_0, is a measure of the relative fragmentation cross-section of the complex. It is safe to assume this is equal to the relative absorption cross-section, σ_{rel}, and provides a reliable value for the absorption of C_{60}^{+} itself. The results shown in Extended Data Figure 2 indicate that all complexes absorb at 9632.7(1) or 9577.5(1) Å. This supports the argument that, after many collisions with He in the trap, only one structural isomer remains, as discussed in the main text. The relative cross-sections for four bands are presented in Extended Data Table 1. The influence of power broadening is shown in Extended Data Figure 3.

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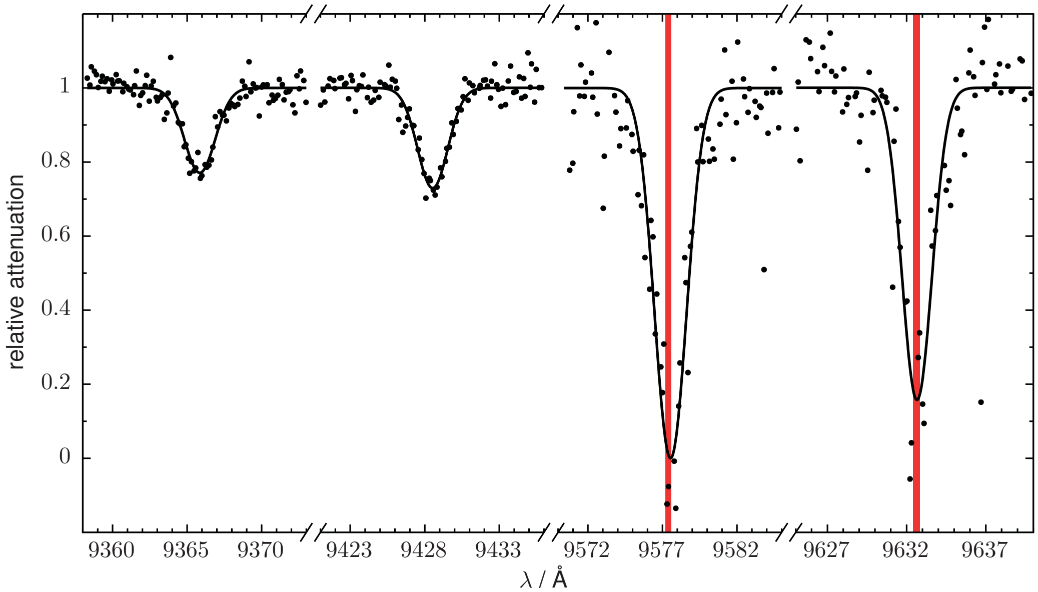

Figure 1 Gas phase laboratory spectra at 5.8 K The spectra were recorded by monitoring the depletion on the $C_{60}^{+} - \mathrm{He}$ mass channel. Gaussian fits to the experimental data (circles) are represented by solid lines. The intensities of the bands have been scaled by the measured relative absorption cross-sections. The fit parameters are given in Extended Data Table 1. The vertical red lines are the rest wavelengths, 9577.4(2) and 9632.6(2) Å, of two DIBs reported in ref. [4], and the width of the lines is given by the uncertainty.

Extended Data Figure 1 $C_{60}^{+}-(He)_2$ spectrum This was recorded by monitoring the depletion on the $C_{60}^{+}-(He)_2$ mass channel. A Gaussian fit to experimental data (circles) is represented by the solid line. The fit gives a band maximum at 9632.8(1) Å and a FWHM of 3.6(2) Å.

Extended Data Figure 2 Relative cross-section measurement a, Fragmentation of $C_{60}^{+}-He$ as a function of laser power at 9632 Å. **b**, Fragmentation of $C_{60}^{+}-He$ as a function of laser power at 9577 Å. Experimental data (circles) have been corrected for the number of background ions appearing at m/z 724 (e.g. $^{13}C_4^{12}C_{56}$). Fits (solid lines) to Equation 2 (Methods) provide information on the relative absorption cross-sections and indicate that all trapped ions interact with the laser.

Extended Data Figure 3 Influence of laser power on the 9577.5 Å band. Gas phase spectrum recorded by monitoring the depletion on the $C_{60}^{+}-He$ mass channel using 1.5 mW (black) and 14 mW (red). Gaussian fits to experimental data (circles) are represented by solid lines, and give FWHM of 2.5(2) and 4.1(2) Å at 1.5 and 14 mW, respectively. The dashed line shows a Gaussian with a FWHM of 2.5 Å

Extended Data Table 1: **Gas phase band maxima, widths and relative absorption cross-sections** The wavelengths, FWHM and standard deviations are determined from fits to the $\mathrm{C_{60}^{+} - He}$ fragmentation spectra using a single Gaussian function. The experimentally determined relative absorption cross-sections are a measure for the relative intensities with an estimated uncertainty of around 20 %.