



The presence of C_{60}^+ in space

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ARTICLE INFO

Article history:

Received 20 June 2018

Received in revised form 4 September 2018

Accepted 13 September 2018

Available online 17 September 2018

Keywords:

Spectroscopy

Ion traps

Interstellar

Fullerenes

Diffuse interstellar bands

ABSTRACT

Experiments in mass spectrometry carried out during the 1980s led to the discovery of the fullerenes. The underlying aim behind these was to understand the formation of carbon chains identified in the interstellar medium some years earlier by radioastronomy. The stability of the discovered C_{60} cage structure led immediately to speculation concerning its role in the context of the diffuse interstellar bands, a set of several hundred optical absorptions observed in the spectrum of reddened star light. The identities of the molecular carriers responsible for these have remained elusive for a century. In 2015, laboratory measurements carried out using a cryogenic ion trap led to the confirmation that C_{60}^+ is responsible for two of the unidentified absorption bands, providing the first clue as to their origin. In this contribution we focus on the experiments that led to this identification. The consequences of this and for other molecules present in such environments is discussed.

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1. Introduction

Spectroscopy of C_{60}^+ and its discovery in interstellar space begins with developments in mass-spectrometry, as appropriate for this journal. Time-of-flight mass-spectra of laser vaporized graphite showed the unusual prevalence of the $m/e = 720$, $^{12}C_{60}^+$ peak, and resulted in the proposal that it is due to the very stable football-structure [1]. This led to the first discussion of the relevance of the electronic absorption spectrum of C_{60} [2] to the now hundred year old astronomical enigma of the diffuse interstellar bands (DIBs) [3].

After the isolation of macroscopic quantities of C_{60} [4] its icosahedral symmetry was confirmed by ^{13}C NMR (nuclear magnetic resonance), the four allowed infrared bands and a crystal structure [4]. Whereas the absorption spectrum of C_{60} was readily obtained in both solid and solution phases, there remains to date only two measurements of cold C_{60} in the gas phase. The first was recorded in a supersonic free jet of laser vaporized graphite using resonant two-

photon ionization for detection [5]. The sensitivity of the approach relies on mass-spectrometry, by counting

C_{60}^+ ions produced with laser photons. Unfortunately the wavelength calibration of this spectrum is imprecise and it has only been reproduced in the laboratory once, using a continuous source of C_{60} with a 100 K vibrational temperature [6], after nearly 30 years. The vibronic pattern is, however, similar to absorption spectra reported in later studies by embedding C_{60} in both helium droplets [7] and neon matrices [8].

The driving force behind the measurement of the gas-phase spectrum of C_{60} was to compare it with astronomical data on DIBs [9]. This could only be partly done [10]; the lowest energy discrete weak bands appearing around 6000 Å still lack the precise wavelengths required, whereas the more intense absorptions below 4000 Å are broad. One of the discoverers of the C_{60} football-structure, H.W. Kroto, realised that in interstellar space it may be its cation that is important, and thus the electronic absorption spectrum of C_{60}^+ will be required [11]. With the availability of C_{60} sample several years later, this became a goal.

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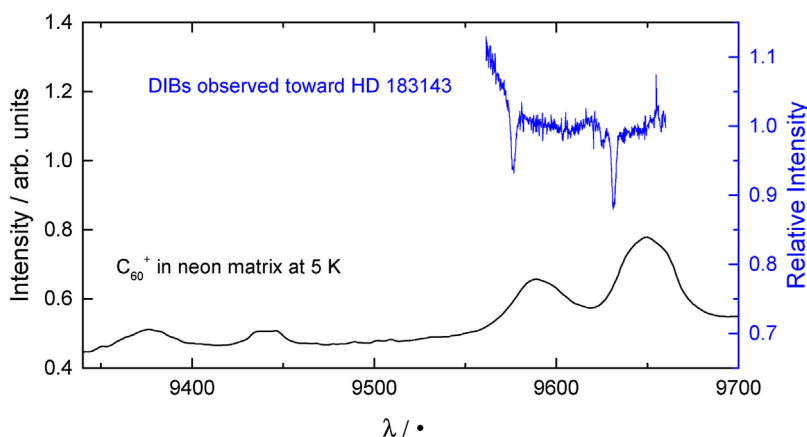


Fig. 1. Electronic absorption spectrum of C_{60}^+ recorded in a neon matrix at 5 K in 1993 (black) compared with two diffuse interstellar bands (blue) reported in 1994 [17]. The astronomical data shown are from a later study by the same authors with a higher S/N ratio than in the initial report [18].

In 1989 we reported a new approach to study the electronic absorption spectra of mass-selected ions [12], though not in the gas-phase but in an environment close to it: neon matrix at 5–6 K. Data obtained by this method are not good enough for a direct comparison with astronomical observations due to the perturbation caused by the surrounding neon atoms: for infrared frequencies this is just a few wavenumbers but for electronic transition involving different states this can be up to 100–150 cm^{-1} [13]. On the other hand for many aspects in chemistry, such a perturbation is not a major concern as the essential spectroscopic features are manifested and elucidate the electronic structure. Hence the widespread use of matrix isolation to study the infrared and electronic spectra of transient species. The limitation of the technique is that usually a number of molecules are concomitantly present in the matrix and thus the overlapping spectra have to be disentangled by laborious chemical means. This can be avoided by mass-selection, though isomers may still be present.

Thus in the absence of a means to measure the electronic spectrum of C_{60}^+ in the gas-phase we obtained one in a neon matrix at 5 K in the 1990s [14]. An important technical aspect of this was the use of a waveguide method to sample a 100–200 μm neon matrix containing the mass-selected ions, by propagating light at small angles of incidence through the thin part. Such a wafer can be built up in 1–2 h using nA currents resulting in ion densities of around 10^{16} cm^{-3} , which is sufficient for detection in a path-length of 2–3 cm.

The obtained absorption spectrum of C_{60}^+ shows a distinct first electronic transition in the near infrared with origin band at 9645 Å. The next electronic transitions are more intense broad absorptions to shorter wavelength than 4500 Å. This was not the first observation of the electronic spectrum of C_{60}^+ : it was initially reported in glassy matrices which resulted in broad absorptions even for the near infrared transition [15] and quite shifted from the neon matrix wavelength. This was followed by a measurement in argon matrices [16], which was better resolved, but still too perturbed to be useful for astronomical purposes. In a neon matrix the transition energy shifts relative to the gas-phase are much smaller. The data on a number of organic cations that were measured both in neon and in the gas-phase enabled us to predict in 1993 that the origin band of the first electronic transition of free C_{60}^+ should lie in the 9650–9510 Å range [14].

A year later in 1994, the observation of two DIBs in this region was reported and proposed by comparison to the neon matrix data to be due to the presence of C_{60}^+ in diffuse clouds [17]. Subsequent measurements by them [18], and other observational groups [19], confirmed the interstellar nature of these absorptions, rather

than originating from stellar atmospheres. It was invariably pointed out in the articles that the gas-phase spectrum of C_{60}^+ at low temperatures (10–80 K) will be required to confirm or dispel this proposition. This is clearly apparent in Fig. 1 where the absorption spectrum of C_{60}^+ in a neon matrix is compared with the two DIBs. The phonon and site structure causes the broadening of the bands in the solid phase.

2. C_{60}^+ spectrum quest

We embarked on a project to measure a cold gas phase spectrum of C_{60}^+ in the laboratory and achieved this in 2015, after two decades of development of possible approaches. Around the time of the C_{60}^+ absorption measurement in neon, we were conducting gas-phase spectroscopic studies of mass-selected ions with rare gases attached, in particular with helium. We could produce $N_2^+ - He$ at a temperature of around 50 K in an electron impact source coupled with a supersonic free jet. The electronic spectrum of the ionic complex was observed by monitoring the production of N_2^+ following resonant laser absorption at the wavelength of the $B^2\Sigma_u^+ \leftarrow X^2\Sigma_g^+$ transition of N_2^+ [20]. The internal energy provided by the laser photon for electronic excitation is sufficient to dissociate the complex into $N_2^+ + He$. This took place in a quadrupole ion guide. The spectrum showed rotational structure as for bare N_2^+ ; in fact within the resolution of the laser (0.2 cm^{-1}) the frequencies coincided with $N_2^+ - He$. The approach was then applied to study the infrared spectra of numerous small ions such as $HCO^+ - He$, $N_2H^+ - He$, by relying on vibrational predissociation in the ground state [21].

At that time, however, we assumed the method used to prepare $N_2^+ - He$ would be inapplicable for $C_{60}^+ - He$ as this requires a high temperature supersonic pulsed valve that also provides a sufficient number of collisions to cool the 174 vibrational modes of C_{60}^+ . A discussion of inefficient vibrational cooling of C_{60} in a molecular beam has been given [22]. In the following decade we instead constructed a more sophisticated apparatus containing a radiofrequency (RF) 22-pole ion trap rather than an ion-guide. The long storage times and low temperatures possible ensure that cold ions and also complexes with helium can be produced *in situ* in the ion trap. Both in the construction and use of RF ion guides and traps for spectroscopy we were guided throughout the years by D. Gerlich [23].

The first objective was to show that the internal degrees of freedom – vibrations and rotations – of the confined ions can be cooled and equilibrated at low temperature. Whereas in supersonic expansions rotational temperatures of a few K can be achieved even for ions produced by electron impact, vibrational relaxation

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