Communication

Synthesis and Spectroscopy of Buckminsterfullerene Cation $\text{C}_{60}^+$ in a Cryogenic Ion Trapping Instrument

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Abstract: The assignment of several diffuse interstellar bands in the near-infrared to $\text{C}_{60}^+$ ions present at high abundance in space has renewed interest in the astrochemical importance of fullerenes and analogues. Many of the latter have not been produced in macroscopic quantities, and their spectroscopic properties are not available for comparison with astronomical observations. An apparatus has been constructed that combines laser vaporisation synthesis with spectroscopic characterisation at low temperature in a cryogenic trap. This instrument is used here to record the electronic absorptions of $\text{C}_{60}^+$ produced by laser vapourisation of graphite. These are detected by (helium tagged) messenger spectroscopy in a cryogenic trap. By comparison with spectra obtained using a sublimed sample of Buckminsterfullerene, the observed data show that this isomer is the dominant $\text{C}_{60}^+$ structure tagged with helium at $m/z = 724$, indicating that the adopted approach can be used to access the spectra of other fullerenes and derivatives of astrochemical interest.

Keywords: laboratory astrochemistry; fullerenes; interstellar molecules; cryogenic ion traps; diffuse interstellar bands; electronic spectroscopy

1. Introduction

The discovery of fullerenes in 1985 resulted from attempts to simulate circumstellar conditions to see whether they promote the formation of long carbon-chain molecules detected by radioastronomy in dense clouds [1]. Ever since, speculations have been made about the role of this carbon allotrope in the context of the diffuse interstellar band (DIB) enigma. These are absorption features in the visible to near-infrared regions that are observed in the spectra of stars viewed through interstellar clouds. The molecules responsible remain (mostly) unidentified despite the detection of the first DIBs around 100 years ago [2].

In the early 1990s, condensed phase experiments using matrix isolation spectroscopy identified electronic absorptions of $\text{C}_{60}^+$ in the near infrared [3–6]. Shortly after, this spectral region was observed toward reddened stars and two interstellar features were found [7] lying within the wavelength range that cold, gas phase, $\text{C}_{60}^+$ was predicted to absorb [6]. The proposed assignment [7,8] of two DIBs at 9577 and 9632 Å to $\text{C}_{60}^+$ present in diffuse clouds stimulated laboratory efforts to obtain spectroscopic data in the gas phase that would enable direct comparison with astronomical data. In 2015, experiments using a cryogenic 22-pole ion trap, in which gas phase $\text{C}_{60}^+$ ions were cooled to internal temperatures below 10 K, were reported. These revealed a striking match to the 9577 and 9632 Å DIBs, thus providing strong evidence for the presence of $\text{C}_{60}^+$ in the interstellar medium (ISM) [9]. Moreover, additional vibronic bands in the laboratory spectrum were identified [9,10] and interstellar absorptions at the corresponding wavelengths observed [11]. These intrinsically weaker features were also recently detected using the Hubble Space Telescope, in data that are free from telluric H$_2$O absorptions in this spectral region [12,13]. In addition, laboratory studies using a different technique, by embedding $\text{C}_{60}^+$ ions in helium droplets,

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provided confirmation of the spectroscopic characteristics obtained from ion trapping experiments [14,15]. The topic is the subject of several recent reviews [16–18].

An important finding from these studies is the remarkable abundance of $C_{60}^+$ in diffuse clouds, which is found to be similar to that of diatomics CH and CH$^+$ [11]. Its high column density, $N(C_{60}^+)=2 \times 10^{13}$ cm$^{-2}$ toward HD 183143 [10], suggests that there may be a significant number of other fullerenes and analogues present in the ISM. In addition, $C_{60}$ was detected earlier [19,20] in various nebulae (see [21] and references therein) by emission of infrared radiation. Recently, laboratory infrared spectra of $C_{60}^+$, $C_{60}H^+$, and $C_{70}H^+$ were also reported and compared with observations [22–24].

In the context of their electronic transitions and the DIBs, fullerene analogues containing cosmically abundant atoms have long aroused interest [25]. Evaluation of their astrochemical significance, however, awaits measurement of their spectroscopic properties in the gas phase at low temperature, which is necessary for direct comparison with observational data in the visible. A prerequisite to obtaining such data is their synthesis. Many fullerenes and analogues have not yet been produced and isolated in macroscopic quantities, and lack a traditional organic chemistry synthesis route. An exception is the endohedrals containing rare gas atoms or small molecules inside the $C_{60}$ cage that have been synthesised using a “molecular surgery” approach (see, e.g., [26] and references therein), of which the electronic transitions of H$_2$@C$_{60}^+$ and He@C$_{60}^+$ were recently reported [27,28].

The generation of some analogues such as endohedral metallofullerenes in the gas phase by laser vaporisation has been reported following analysis of mass spectra (e.g., [29] and references therein). Following their synthesis, a major challenge associated with spectroscopic detection is cooling to low temperatures such that only the lowest vibrational level in the ground electronic state is populated. This is especially important for comparison with astronomical observations, where nonpolar species reach 30–80 K. Due to its 174 vibrational degrees of freedom, cooling $C_{60}$ is a formidable experimental task, and traditional methods such as supersonic expansions suffer from the limited number of collisions [30]. On the other hand, buffer gas cooling has been successful at relaxing the internal modes of $C_{60}^+$ in an ion trap [9], and more recently those of $C_{60}$ in a collision cell [31]. In the ion trap study, number densities of helium buffer gas of $4 \times 10^{15}$ cm$^{-3}$ coupled with an interaction time of $>500$ ms led to millions of collisions with cryogenic helium. This technique was exploited to prepare $C_{60}^+$ ions for spectroscopic characterisation, finally leading to its confirmation as the carrier of the 9577 and 9632 Å DIBs [9].

In this contribution, a cryogenic ion trapping instrument is used to spectroscopically demonstrate the formation of the Buckminsterfullerene cation, $C_{60}^+$, as the dominant structure with $m/z=720$ generated by laser vapourisation of graphite, paving the way to studies on other fullerenes and analogues of astrochemical interest. The experiment is described in Section 2, results are compared with previous work using sublimed C$_{60}$ in Section 3, and conclusions are given in Section 4.

2. Experimental

Ions are generated by laser vaporisation of a graphite rod (99.997%, particle size: 20–100 µm) using the frequency-tripled emission of a pulsed Nd:YAG laser source. Pulses of 20 mJ in energy and 7 ns in duration are focused onto the rod as it is swept by a 50 µs-long pulse of helium gas. Products of the interaction between the laser-induced plasma and the helium gas are expanded into a high vacuum chamber. Both the laser and the piezo valve are pulsed at a repetition rate of 10 Hz. The species produced are collimated by a skimmer before entering the first quadrupole mass filter of the laser vapourisation-diffuse interstellar band-solid quadrupole trap (LV-DIB-s4PT) instrument. A full description of the apparatus is given in [32].

For spectroscopic measurement, ions with $m/z=720$ generated from 5 laser pulses are accumulated in the s4PT trap. Here they undergo collisions with cryogenically cold He atoms (nominal temperature, $T_{\text{nom}}=4.2$ K), present with a number density of $10^{15}$ cm$^{-3}$, during the first 500 ms of the trapping period. These conditions result in the formation of
weakly bound complexes of \( C_{60}^+ \) with helium, \( C_{60}^+ - \text{He}_n \). After pumping out the buffer gas, the ion cloud is exposed to radiation from a continuous wave diode laser, using a mechanical shutter to control the exposure time, before the trap contents are extracted and analysed by mass spectrometry. The number of ions on alternate trapping cycles are monitored with \( N_i \) and without \( N_0 \) laser radiation (<1 mW) to account for fluctuations in the number of ions stored. Typical values of \( N_0 \) in these experiments were 500–1000.

3. Results and Discussion

A mass spectrum showing the distribution of \( C_{60}^+ \) synthesised in the source is shown in Figure 1a. These data were obtained by operating the first quadrupole in the LV-DIB-s4PT instrument in transmission mode and guiding the ions to the second mass spectrometer. In this mass range, the most intense peaks are those \( C_{60}^+ n \) that possess even \( n \). This intensity pattern, with the most abundant peak at \( m/z = 720 \), followed by other prominent ones separated by \( C_2 \) units, is characteristic of the formation of fullerenes.

![Figure 1](image_url)

Figure 1. (a) Mass spectrum of positive ions generated by laser vaporisation of graphite. (b) Contents of trap following storage of \( C_{60}^+ \) ions in cold and dense helium buffer gas. (c) Mass spectrum obtained following irradiation of stored ions at \( \bar{\nu} = 10,438 \text{ cm}^{-1} \), revealing dissociation of \( C_{60}^+ - \text{He} \).

Presented in panel (b) of Figure 1 is a mass spectrum of the trap contents following ion storage at 4.2 K in dense \( (10^{15} \text{ cm}^{-3}) \) helium buffer gas. This demonstrates the formation of weakly bound \( C_{60}^+ - \text{He} \) appearing at \( m/z = 724 \) which are used to obtain spectroscopic information by action spectroscopy. Tagging \( C_{60}^+ \) ions with He enabled the electronic spectra of \( C_{60}^+ - \text{He}_n \) complexes to be recorded, from which the absorption band wavelengths for \( C_{60}^+ \) were determined [9,33]. In [9], a commercial sample of \( C_{60} \) was sublimed and ionised by 50 eV electron impact. The resulting \( C_{60}^+ \) ions were loaded into the trap and complexes were formed by collisions with cryogenically cold helium buffer gas. Independently of the synthesis procedure, electronic excitation of \( C_{60}^+ - \text{He} \) by absorption of a \( \sim 1.3 \text{ eV} \) energy photon breaks the weak bond between the fullerene ion and the helium atom. The spectrum is thus obtained by monitoring attenuation of ions with \( m/z = 724 \). A mass spectrum of the trap contents in this work, following irradiation of the ion cloud at \( \bar{\nu} = 10,438 \text{ cm}^{-1} \), is shown in panel (c) of Figure 1. This demonstrates dissociation of the synthesised \( C_{60}^+ - \text{He} \) complexes.

The near-infrared absorptions of \( C_{60}^+ \) have been assigned to the lowest energy \( ^2E_{1g} \leftarrow X^2A_{1u} \) electronic transition (in \( D_{5h} \)). Recent theoretical work indicates that \( C_{60}^+ \) undergoes a Jahn-Teller distortion from the \( D_{5h} \) minimum such that the upper \( ^2E_{1g} \) state is split into two components with \( A_g \) and \( B_g \) symmetry (in \( C_{2v} \)), leading to two transitions separated by \( 41 \text{ cm}^{-1} \) (see Figure 3 in [34]). Transitions from the \( A_u \) ground electronic state to these components are believed to be responsible for the absorption bands of \( C_{60}^+ \) at 10,378 and 10,438 cm\(^{-1}\).

An example spectrum from previous experiments on a sublimed sample of \( C_{60} \) is presented in Figure 2 (top trace). These data are those reported in [35], and show the two strongest absorption bands in the electronic spectrum near 10,438 and 10,378 cm\(^{-1}\). These \( ^{12}C_{60}^+ - \text{He} \) absorptions have widths of approximately 2 cm\(^{-1}\) which is caused by
the ∼2 ps lifetime of the excited electronic state. Also shown in Figure 2 (bottom) are data reported here for $^{12}$C$_{60}^+$−He following helium tagging of $m/z = 720$ ions produced by laser vapourisation of graphite. The spectrum was recorded by monitoring the attenuation $(1-N_i/N_0)$ of ions with $m/z = 724$. As is evident from inspection of Figure 2, the two sets of data are equivalent, with absorption band profiles that are almost superimposable, aside small differences due to the signal-to-noise ratio.

Figure 2. Origin bands of the $^2B_g ← X^2A_u$ and $^2A_g ← X^2A_u$ electronic transitions of C$_{60}^+$−He near 10,378 and 10,438 cm$^{-1}$, respectively. The experimental data obtained with laser vapourisation of graphite (circles) have been fit with Lorentzian profiles (blue line). Also shown are previous data (solid line, top) from [35] following experiments with a sublimed sample of C$_{60}$.

Previous experiments (see Figure 3 in [9]) indicate that the 10,378 and 10,438 cm$^{-1}$ transitions arise from the same structural isomer of C$_{60}$ as indicated by near complete attenuation of ions with $m/z = 724$ following irradiation of the ion cloud on resonance. In the present work, increasing the laser fluence led to saturation of the number of ions with this $m/z$ at an attenuation $(1-N_i/N_0)$ of ∼80% (not shown), leading to the conclusion that the majority of C$_{60}^+$ ions tagged with He in the trap are the distorted ($D_{5d}/C_{2h}$) soccer ball form. The structure(s) of the remaining 20% are unknown; however, their spectroscopic properties could be explored in future studies. Other, non-isolated pentagon cage structures have been reported in [36].

4. Conclusions

Buffer gas cooling and spectroscopic characterisation in a cryogenic ion trap have been used to demonstrate the formation of the Buckminsterfullerene cation C$_{60}^+$ by laser vapourisation of graphite. The $^2B_g ← X^2A_u$ and $^2A_g ← X^2A_u$ electronic band origins near 10,378 and 10,438 cm$^{-1}$ were detected by messenger spectroscopy, and found to be consistent with results of experiments using a sublimed sample of C$_{60}$, indicating that of the C$_{60}^+$ ions tagged with helium in the trap ($m/z = 724$), the (slightly distorted) $D_{5d}/C_{2h}$ soccer ball isomer dominates. Although the formation of the Buckminsterfullerene cation C$_{60}^+$ by laser vapourisation is well established, the presented data demonstrate that this synthesis route provides a sufficient yield of ions to allow spectroscopic characterisation in an ion trap. These proof-of-principle results are a first step toward obtaining the electronic absorptions of other fullerene cations and analogues that are sought after in the context of the enigmatic diffuse interstellar bands. It is thus anticipated that the adopted approach of combining laser vapourisation synthesis with spectroscopic characterisation in a cryogenic trap can enable data on a variety of structures that have not been produced in
macroscopic quantities to be recorded at low temperature to enable direct comparison with astronomical observations.

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