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Spectroscopy of astrophysically relevant ions in traps

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ABSTRACT

The detection of molecules in the interstellar medium relies on the comparison between observational and laboratory data recorded under relevant conditions. In this contribution, the use of cryogenic ion traps to obtain low temperature spectra of gas-phase ions of astrophysical relevance is reviewed. By exploiting the unique properties of these devices, the requisite spectroscopic data that led to the identification of C_{60}^+ as the first carrier of the enigmatic diffuse interstellar bands could be measured. These experiments are discussed, along with electronic transitions of other fullerenes, and recent approaches to synthesize and characterize molecular ions of long-held astrochemical interest.

KEYWORDS

cryogenic ion traps, interstellar molecules, electronic spectroscopy, fullerenes, diffuse interstellar bands

1. Introduction

The first molecules detected in the interstellar medium (ISM) were the diatomics CH, CH^+ and CN. These were observed between the late 1930s and early 1940s in regions through which starlight penetrates by absorption spectroscopy [1–5]. The subsequent introduction of radio-techniques led to the identification of OH and NH_3 in

so-called dense clouds by emission in the 1960s [6–8]. This followed predictions made by Townes on the detectability of these molecules [9], and observations of H_2O [10] and H_2CO [11] came soon after. The presence of cyanopolyacetylenes HC_3N , HC_5N , HC_7N and HC_9N was revealed in the 1970s [12–15], and stimulated laboratory experiments that ultimately led to the discovery of a new allotrope of carbon known as fullerenes [16]. Today, the number of molecules identified by such methods is around 200 [17]. However, because a permanent electric dipole moment is required, and the rotational partition function increases with size and complexity, the detection of large, high symmetry structures using radio-techniques is not possible. A consequence of this is that most of the discovered molecules are small, polar ones containing 13 or fewer atoms.

Commonly cited evidence for the presence of larger molecules in regions of dust and gas illuminated by UV radiation is the unidentified infrared bands (UIB). These are broad features observed in emission at wavelengths of 3, 6.2, 7.7, 8.6, 11.2, 12.7, and $16.4\ \mu\text{m}$ [18–20]. They coincide with the C – C and C – H vibrational frequencies of aromatic molecules, leading to the proposal that they are the fingerprints of polycyclic aromatic hydrocarbon (PAH) or similar type structures [21, 22]. Much work has been done in this area (see, for example, Refs 23–27), however, to date, not a single PAH has been identified, and it appears that the broad, overlapping nature of the UIBs precludes detection of individual molecular carriers. Only recently has benzonitrile, $\text{C}_6\text{H}_5\text{CN}$, been detected by radio-methods. Its column density in TMC 1 was found to be a factor of 5 lower than HC_9N [28].

One of the most perplexing problems in spectroscopy and observational astronomy is the diffuse interstellar bands (DIBs). These are absorption features appearing in the optical region of the spectra of stars that lie beyond, and are viewed through, diffuse clouds. Their history dates back around one hundred years and today the number of detected DIBs is around 500. Some of the first observations of them were made by Mary Lea Heger [29] and in the intervening period many hypotheses (see, e.g. Refs. 30, 31) have been advanced concerning the nature of the unknown carriers. Their early history has been nicely described by McCall [32]. The DIBs cover a range of wavelengths from about $4000\ \text{\AA}$ to the near-infrared, as illustrated in Figure 1 [33].

They each possess different intensities and have widths which range from tenths to tens of Ångströms. As is evident from this Figure, some of these are strong, absorbing up to 30 % of the intensity of star light at a given wavelength. One hint toward their molecular origin came from a careful examination of the absorption band profiles. Some are found to resemble the unresolved rotational envelopes of electronic transitions of gas-phase polyatomics [34]. Others display Lorentzian lineshapes due to homogeneous broadening [35].

The consensus over the last decades is that they are likely to be the spectral fingerprints of gas-phase organic molecules [36]. In order to advance this hypothesis, laboratory spectroscopy is required. Several experimental techniques have been developed and applied over decades with the goal of obtaining gas-phase spectra of target molecules at temperatures relevant to the ISM to compare with astronomical observations (see Ref. 37 and references therein). In 2015 experiments carried out using a cryogenic 22-pole ion trap provided convincing laboratory evidence that C_{60}^+ is a DIB carrier [38]. In addition to revealing the first answer to the century old and much cited puzzle of the DIBs, C_{60}^+ was shown to have a remarkable abundance, similar to diatomics CH and CH^+ in these environments [39], reigniting long-held interest in the astrochemical importance of fullerenes and their analogues [40].

This article focuses on the spectroscopy of astrochemically relevant ions in traps and is organized as follows. The field is introduced in Section 2 and some interesting recent developments are described. Experiments that led to the identification of C_{60}^+ as DIB carrier are reviewed in Section 3. Recent laboratory results obtained by combining methods to synthesize and characterize species that have not yet been isolated in macroscopic quantities are presented in Section 4. Finally, a brief discussion of future opportunities is given in Section 5.

2. Cryogenic traps for spectroscopy

The popularity of variable temperature radiofrequency traps for spectroscopy as well as reaction dynamics in several groups is built on the pioneering work of Ger-

lich [41, 42]. In such devices, ions can be stored and probed using tunable laser radiation [43]. Typical trapping instruments (see Figure 2) contain several modules for producing, mass-selecting, confining, interrogating and finally detecting charged particles. The central part of an apparatus is a radiofrequency trap, mounted onto a cryostat, in which the ions are confined, cooled and probed with either collisions or photons. Low temperatures and long storage times allow chemical reactivity and photoinduced processes to be probed at temperatures of just a few Kelvin. An example of the sensitivity afforded by this technology is the ability to measure extremely small ($10^{-16} \text{ cm}^3 \text{ s}^{-1}$) rate coefficients for radiative association processes [44], a reaction mechanism of significant astrochemical importance (see, for example, Ref. 45).

In a typical experiment, ions generated in the source chamber are mass-selected using a quadrupole mass spectrometer, turned through 90° and injected into the trap. Here they are confined in the radial direction using an inhomogeneous radiofrequency field and in the axial direction by two cylindrical electrodes. The internal degrees of freedom of the trapped species are cooled *via* inelastic collisions with buffer gas at the temperature of the trap walls, the latter reaching 3 K or lower. In spectroscopic experiments, the confined ions are subjected to tunable laser radiation before the trap contents are extracted and analyzed using a quadrupole mass spectrometer and a Daly detector.

A major advantage of traps over more traditional methods such as supersonic expansions is the flexible timescale for cooling and probing. In the latter technique, the limited number of collisions in the expansion, while usually successful at relaxing the rotational modes, does not always lead to cooling of all the vibrations to their ground states. This is particularly true for very large molecular ions such as C_{60}^+ , which has 174 vibrational degrees of freedom. Another remarkable aspect is the sensitivity that can be achieved by counting (almost) all mass-selected ions at the end of the trapping period. For example, it is possible to obtain spectroscopic data on just a few hundred stored ions, through what is referred to as action spectroscopy.

The need for such an approach can be understood as follows. In an experiment an ensemble of some thousand ions confined in a 22-pole trap interacts with laser radiation. Their column density in the trap is very small, and the resulting attenuation

of laser light therefore extremely weak. As an example, for C_{60}^+ ions irradiated in the near infrared the attenuation of light would be just 5×10^{-11} [39]. Such a value is not directly detectable through monitoring the transmitted intensity, however, action spectroscopy, which relies on a signature of this excitation being translated into a change in the mass-spectrum, can be used to obtain the spectroscopic data. Examples include laser induced dissociation (LID) [46] and laser induced reaction (LIR) [47, 48]. The former method involves the fragmentation of the target molecular ion, which often requires absorption of several photons. The latter LIR approach exploits differences in the chemical reactivity of the ion following photon absorption relative to that in its ground state. In this case, monitoring the reactivity as a function of the photon wavelength provides the requisite spectroscopic information. However, both of these methods have some disadvantages, for example, LID requires the molecular ion to fragment, making it difficult to detect species with slow fragmentation rates, whereas LIR requires identification of a suitable chemical reaction.

Recent advances in the spectroscopy of trapped ions came with the achievement of temperatures of a few degrees Kelvin and the use of dense ($10^{15} - 10^{16} \text{ cm}^{-3}$) helium buffer gas. Under these conditions it became possible not only to cool the internal degrees of freedom of large molecular species to temperatures prevailing in astrochemical environments, but also to synthesise *in situ* weakly bound ion-induced dipole complexes of organic ions with helium (e.g. $C_{60}^+ - \text{He}$). This has given rise to new possibilities in spectroscopy, for example, due to the weak binding energies of these complexes, single photon excitation of vibrational and/or electronic motion leads to fragmentation. A relatively straightforward approach has been demonstrated in which almost 100 % of complexes can be dissociated [49]. This has been used since the 1990s to spectroscopically investigate small ionic complexes with helium formed in supersonic expansions [50].

Another recent approach to obtaining spectra of cold molecular ions involves hindering the *in situ* formation of complexes like $N_2^+ - \text{He}$ through resonant excitation of the bare (N_2^+) molecular ion. This has been termed laser induced inhibition of complex growth (LIICG), and in this example yielded the spectrum of N_2^+ rather than that of the $N_2^+ - \text{He}$ complex. Laser excitation of the $A^2\Pi_u \leftarrow X^2\Sigma_g^+$ electronic transition

of cold N_2^+ was shown to reduce the number of observed $\text{N}_2^+ - \text{He}$ complexes by suppressing their formation through the creation of energised N_2^{+*} molecules [51]. The applicability of this method to other spectral regions was subsequently demonstrated through infrared measurements of H_3^+ and CH_5^+ [48, 52].

Early spectroscopic investigations were carried out using 22-pole traps. With these geometries the effective potential has steep walls, leading to a wide, nearly field free region for optimum cooling of the translational energy of the ion [53]. The final internal temperature of ions achieved is given by the mass-weighted average of the translational temperature of the ions and the buffer gas, $T_{\text{int}} = (m_{\text{He}}T_{\text{ion}} + m_{\text{ion}}T_{\text{He}})/(m_{\text{ion}} + m_{\text{He}})$ [43]. In the case of heavy ions such as C_{60}^+ stored in helium, internal temperatures below 10 K are reached, even for a high ion translational temperature. Many studies have been able to spectroscopically demonstrate the relaxation of rotational and vibrational degrees of freedom (see, for example Ref. 54 and references therein). In a 22-pole trap, the region explored by the confined ions is typically larger than the diameter of the laser beam used to probe them. Moreover, an attractive patch potential on one of the electrodes can lead to the ions spending longer outside the laser beam than assumed. This has the potential to cause large uncertainties in the experimental determination of absolute cross-sections. For these reasons, several linear quadrupole traps have been developed recently to obtain spectra of heavy ($m_{\text{ion}} > m_{\text{He}}$) ions, and enable accurate measurement of absolute cross-sections. By confining the ions to a small cylinder, multiphoton absorption can also be observed, as discussed in Ref. [55].

The cooling of ions not only simplifies spectra but also provides data that is appropriate for comparison with astronomical observations. Action spectroscopy in traps has been used to observe rotational [56] as well as vibrational [57] transitions of molecular ions of astrochemical interest. In the following sections of this article the focus is on electronic spectroscopy, particularly studies involving the author, and the interested reader is referred to several excellent reviews covering other spectral regions and applications of these methods with similar instruments (Refs. 58–67).

3. C₆₀⁺ spectroscopy and identification of DIBs

3.1. Background

The fullerenes were discovered following experiments carried out with the aim of recreating, in the laboratory, conditions that could give rise to the formation of carbon chains in stellar outflows. Motivation for these activities came from the detection of cyanopolyacetylenes by radio-methods some years earlier, leading to the question of whether these molecules are formed in stellar atmospheres, and survive in the ISM, or are directly synthesised in the ISM itself. As a test of the former hypothesis, efforts were made to simulate the conditions in circumstellar environments.

In the 1985 experiment, 532 nm radiation from the second harmonic of a Nd:YAG laser was used to produce carbon clusters from a rotating graphite disk. The neutral molecules were ionized in a helium expansion and detected *via* time-of-flight mass spectrometry. The results showed a distribution where, for mass-to-charge ratios (m/z) of greater than 490, only species containing an even number of carbon atoms were observed. Moreover, a slightly enhanced peak at $m/z = 720$, and also one at $m/z = 840$, was seen. These “clusters” are now known as fullerenes, an allotrope of carbon in addition to the previously identified graphite and diamond. It was immediately recognized that this may have implications for the DIB enigma and, in 1987, Kroto highlighted the astrophysical importance of the singly charged cation C₆₀⁺, writing “The present observations indicate that C₆₀ might survive in the general interstellar medium, probably as the ion C₆₀⁺ protected by its unique ability to survive processes so drastic that most, if not all, other known molecules are destroyed” [68]. This conjecture was subsequently shown to be correct.

The electronic spectrum of C₆₀⁺ was measured by several groups [69, 70] using solid-state matrix isolation methods shortly after C₆₀ was isolated in macroscopic quantities [71]. The Maier group recorded the best resolved spectrum in 6 K neon and were able to predict the wavelength range in which gas-phase C₆₀⁺ absorbs [72]. This region was observed through diffuse clouds toward several reddened stars by Foing and

Ehrenfreund [73], who found two interstellar absorptions and suggested that these could be caused by C_{60}^+ . Later observations toward HD 183143 improved the S/N, revealing DIBs at 9577 and 9632 Å that cause $\sim 10\%$ attenuation of star-light at their band maxima [74]. It was pointed out that gas-phase data are required to confirm this assignment, as is clearly evident if one compares the matrix and astronomical spectrum (see Figure 1 in Ref 54). It was not until 2015 that appropriate laboratory results were obtained, following measurement in a cryogenic ion trap, as outlined below [38]. The aim here is not to review all of the reported laboratory and astronomical studies related to C_{60}^+ , as has been done elsewhere [37, 54, 75], but rather to briefly highlight some of the insights gained from ion trapping experiments.

3.2. Gas-phase Spectroscopy

To carry out these experiments, C_{60} was ionized by 50 eV electrons in the source chamber of the ion trapping instrument (see Figure 2). The generated C_{60}^+ were transmitted through a quadrupole mass-filter and injected into a 22-pole ion trap held at 5 K. The stored C_{60}^+ were cooled by collisions with helium buffer gas, present at $4 \times 10^{15} \text{ cm}^{-3}$, and in equilibrium with the temperature of the walls. Under these conditions a few percent of the total C_{60}^+ ions were converted to weakly bound $C_{60}^+ - \text{He}$ complexes *via* ternary association in the three-body process, $C_{60}^+ + 2\text{He} \rightarrow C_{60}^+ - \text{He} + \text{He}$. Due to the size of C_{60}^+ , and the weak interaction with the externally bound helium atom, it was expected that the perturbation to the electronic spectrum of C_{60}^+ would be small and it was thus attempted to record the spectrum by photofragmentation through the loss of the helium atom. The *in situ* synthesis of helium complexes with fullerene ions in cryogenic traps has been described in detail in a recent article by Gerlich *et al.*, which also discusses early ideas about recording IR spectra of molecular ions using this approach [55].

The method exploits the fact that after electronic excitation of $C_{60}^+ - \text{He}$ with a 1.3 eV photon, some of this energy finally makes its way to the weak bond between C_{60}^+ and He and dissociates it. The resulting attenuation can then be monitored through the change in the number of ions with $m/z = 724$. Although the first set of experiments

were carried out with a rather low conversion of primary ions into complexes, they led to the observation of the two strongest absorption bands of $C_{60}^+ - He$ near 9577 and 9632 Å and two weaker ones near 9428 and 9365 Å. As well as providing gas-phase data, these results clarified several important spectroscopic aspects that were uncertain from the matrix and astronomical studies. In particular, they showed that both the 9577 Å and 9632 Å absorptions are caused by one C_{60}^+ structural isomer, and arise from the lowest vibrational level of the same ground electronic state (${}^2A_{1u}$ in D_{5d}). Recent theoretical work assigned these as transitions to two components (2A_g and 2B_g in C_{2h}) of the Jahn-Teller split excited ${}^2E_{1g}$ state, with the next two absorption bands to higher energy involving excitation of the lowest frequency cage vibration ($\sim 230 \text{ cm}^{-1}$) [76]. The widths of the laboratory bands were found to be similar, but slightly narrower, than the interstellar ones, with the appearance of the profile below 10 K caused by internal conversion. It was immediately apparent that the gas-phase data provided a convincing match to the DIBs identified by Foing and Ehrenfreund [38, 73]. Astronomical studies have since revealed several further DIBs due to C_{60}^+ at the wavelengths of the weaker laboratory absorptions [39, 77–79]. A comparison of the latest high S/N experimental data with the 9577 and 9632 DIBs is shown in Figure 3.

Following the initial report, improvements were made to the ion trapping instrument. In particular, a new linear quadrupole trap was constructed [39]. An important aspect of the design is that trap housing is machined from a single piece of copper and directly attached to the cold head. To enable optimal cooling of the quadrupole electrodes they are mounted on this copper box using thin sapphire plates, as indicated in Figure 4. With this geometry, the ion cloud can be constrained to a smaller cylinder to ensure interaction of all ions with laser radiation. The lower trap temperatures achieved following these improvements ($T_{\text{nom}} = 3.7 \text{ K}$) allowed formation and measurement of $C_{60}^+ - He_n$ ($n = 1 - 3$), enabling refinement of absorption characteristics inferred for C_{60}^+ [80, 81], and determination of absolute cross-sections [39]. Many of the experimental details and comparison with astronomical data have been reviewed in Ref. [54].

Absolute fragmentation cross-sections were obtained by irradiation of $C_{60}^+ - He$ as a

function of laser fluence, Φ , and typical data are shown in Figure 4. The unity quantum yield for dissociation leads to identical values for absorption, and the result inferred for C_{60}^+ is $5 \times 10^{-15} \text{ cm}^2$ at 9577 \AA [39]. This enabled determination of the C_{60}^+ column density in interstellar environments without the need to rely on theoretical oscillator strengths. $N(C_{60}^+)$ is related to the absorption cross-section through the simple expression, $\ln(I_0/I)/\sigma$. In observations toward HD 183143, an intensity ratio I_0/I of 0.91 at 9577 \AA was measured [77]. Taking this value, together with the experimentally determined absorption cross-section, leads to $N(C_{60}^+) = 2 \times 10^{13} \text{ cm}^{-2}$. To put this result in context, it is instructive to compare with other known species in these interstellar environments. It turns out that this value is similar to the column densities of diatomics such as CH^+ observed along the same line-of-sight [82].

3.3. Follow-up experimental studies

Due to it being the second most abundant C_{2n}^+ produced under the usual electric arc discharge or laser vaporization synthesis, C_{70}^+ was targeted in follow-up studies. Its electronic spectrum was measured as for C_{60}^+ by photofragmentation of $C_{70}^+ - \text{He}$ complexes synthesised in a cryogenic trap. In the region $7000 - 8000 \text{ \AA}$, assigned to a ${}^2E'_1 \leftarrow {}^2E''_1$ transition in D_{5h} symmetry [83], more than ten overlapping absorptions of equivalent intensity are observed. Although this electronic band falls in the spectral region of relevance for the DIBs, the dilution of its electronic oscillator strength precludes detection because each absorption has a small cross-section ($\sim 10^{-17} \text{ cm}^2$). The conclusion reached in this study is that for a C_{70}^+ column density similar to $N(C_{60}^+)$, the absorptions would lie significantly below the current astronomical detection limits [39].

The 13.6 eV threshold for photons in the diffuse ISM, due to the ionization potential (IP) of hydrogen atoms, led to consideration of the doubly charged cation C_{60}^{2+} , as the process $C_{60}^+ + h\nu \rightarrow C_{60}^{2+}$ is possible on energetic grounds, requiring around 11 eV. There are no transitions of C_{60}^{2+} from its singlet ground state in the spectral range of interest for the DIBs, however, C_{70}^{2+} does possess an electronic band in this region, and is also energetically accessible in the ISM from C_{70}^+ [84]. The gas-phase spectrum, assigned as ${}^3E'_1 \leftarrow X {}^3A'_1$ in D_{5d} [85], was measured by fragmentation of $C_{70}^{2+} - \text{He}$, revealing a simple pattern of an intense origin band and two weaker features

lying several hundred wavenumbers to higher energy. Although the absorption cross-section at the origin band maxima, near 7030 Å, was found to be $2 \times 10^{-15} \text{ cm}^2$, the broad FWHM of 35 Å makes astronomical searches difficult. The predicted depth of an interstellar absorption due to C_{70}^{2+} , based on abundance arguments, is around one half of one percent [86].

The unfavourable absorption characteristics of these species mean that additional data is required before the size distribution of fullerenes in the diffuse ISM can be evaluated. In 2010 infrared emission from a young planetary [87] and reflection [88] nebula identified the presence of C_{60} and C_{70} . It is thus expected that C_{70}^+ should also be a constituent of diffuse clouds, following ionization of C_{70} . Accurate electronic spectroscopy of both C_{60} and C_{60}^- is desired for evaluation of the charge distribution, and subsequent modelling of conditions in the ISM, as discussed in Ref [54]. Recently, gas-phase infrared spectra of $\text{C}_{60}^+ - \text{He}$ [89] and C_{60}H^+ [57] were reported and compared with emission data from astrophysical objects. Unlike C_{60} , which has only four infrared active modes, the situation for these ions is less favourable due to their more complicated spectra and the broad, overlapping appearance of the UIBs.

4. Combining methods for synthesis and characterization

The identification of C_{60}^+ as a DIB carrier, and the discovery of its high abundance in diffuse clouds, provides a strong incentive to obtain electronic spectra of other fullerenes and analogues under conditions relevant to the ISM. Of particular interest are high symmetry species which, like C_{60}^+ , possess a simple absorption pattern. Although there remain open questions concerning its formation, if C_{60} is synthesized in high density and temperature circumstellar regions, one might anticipate the interstellar presence of C_{60} analogues containing other abundant atoms, M. Already in 1992 it was argued that charge transfer transitions of C_{60}^+M species should be associated with large oscillator strengths because charge transfer occurs over a long distance [40].

Recent developments in synthetic chemistry have seen the production of a few endohedral fullerenes containing rare gas atoms or small molecules inside the C_{60} cage [90–

93]. Electronic spectroscopy of $\text{He}@C_{60}^+$ and $\text{H}_2@C_{60}^+$ were recently reported [94, 95], and high quality observational data is required to evaluate their possible presence in the ISM. Aside from these examples, many fullerenes and their analogues have not been isolated in macroscopic quantities. However, with developments in mass-spectrometry that enable their gas-phase synthesis (see, for example, Ref. [96]), and the availability of sensitive methods for spectroscopic characterization in low temperature traps, measurement of their electronic transitions is now feasible.

One approach recently adopted is to generate gas-phase ions by laser vaporization. A source module was constructed and incorporated into the cryogenic ion trapping apparatus, as illustrated in Figure 5. Radiation from a pulsed laser is focussed onto a graphite rod that is simultaneously rotated and translated through a metal block. The laser is synchronised in time with a pulse of helium gas from a piezo valve, and admitted into an orthogonal orifice on the block. A neutral plasma with high ion densities is produced and exits the block through a channel perpendicular to the direction of the laser beam. This undergoes free jet expansion in a high vacuum chamber, encountering a skimmer before entering the prefilter of the first quadrupole mass-spectrometer in the ion trapping apparatus. More details of the source are given in Ref. 97.

In a typical experiment, the chosen C_n^+ is mass-selected by the first quadrupole, and turned through 90° by an electrostatic bender prior to injection into the solid linear quadrupole trap. Here, ions produced by several source laser pulses are accumulated and cooled to cryogenic temperatures by inelastic collisions with helium buffer gas. After pumping out the gas the confined ions are exposed to laser radiation before analysis of the trap contents using a quadrupole mass-spectrometer and Daly detector. The potential of this approach was demonstrated through proof-of-principle experiments on C_6^+ . Mass-selected ions with $m/z = 72$ were injected into the cryogenic trap at 3 K and through interaction with helium buffer gas present at some 10^{15} cm^{-3} , $C_6^+ - \text{He}$ complexes were readily formed. Irradiation of the ion cloud with a pulsed tuneable OPO led to observation of the ${}^2B_2 \leftarrow X {}^2A_1$ electronic transition of the cyclic structural isomer, with origin band near 5700 \AA . This system was chosen for initial experiments because previous 6 K neon matrix study had identified the wavelengths of electronic transitions of both linear and cyclic isomers [98]. Aside from this example, and ion

mobility measurements, little experimental data exists for other carbon cations (see Ref. [99]), however, spectroscopic characterization of structures ranging from the small chains and rings to larger fullerenes in the gas-phase is now proceeding.

5. Concluding remarks

Experimental advances exploiting the unique properties of traps have recently enabled long sought gas-phase spectroscopic data to be obtained on molecular ions of astrochemical interest. The method of tagging cations with helium atoms has recently become routine and, in the case of very large systems the perturbation on the electronic transition can be sufficiently weak that the spectrum is a good approximation to that of the bare ion. For smaller molecular ions the helium tag can more severely disturb the system. Nevertheless, messenger spectroscopy using traps, at least for ions, is now competitive with solid-state techniques such as matrix isolation, in that the wavelength range containing the electronic transitions can be located in a relatively straightforward one-photon experiment. Such a route to obtaining spectroscopic information is extremely useful for species for which little is experimentally known, and can provide the requisite data for later high resolution investigation using other approaches.

Our recent messenger spectroscopy experiments have been carried out using a 5 cm^{-1} bandwidth OPO to rapidly scan from the UV to NIR to locate any strong electronic transitions. Others have shown that even broader lightsources that can be used to obtain overview spectra [100]. Once the appropriate wavelength range is identified, other sensitive action spectroscopy methods can be exploited to record high resolution data. These include LID, LIR and LIICG as discussed above. For small ions such as C_5^+ and C_6^+ recently investigated in our laboratory, experiments have shown that 2-colour fragmentation can be observed and the spectrum of the bare ion obtained [101]. With the ability to combine methods for the synthesis of molecules at high temperatures relevant to circumstellar shells with spectroscopic characterization in a cryogenic trap, low temperature gas-phase data on carbonaceous species of long-held astrochemical interest are now within reach. Experiments in this direction are

currently underway in our laboratory.

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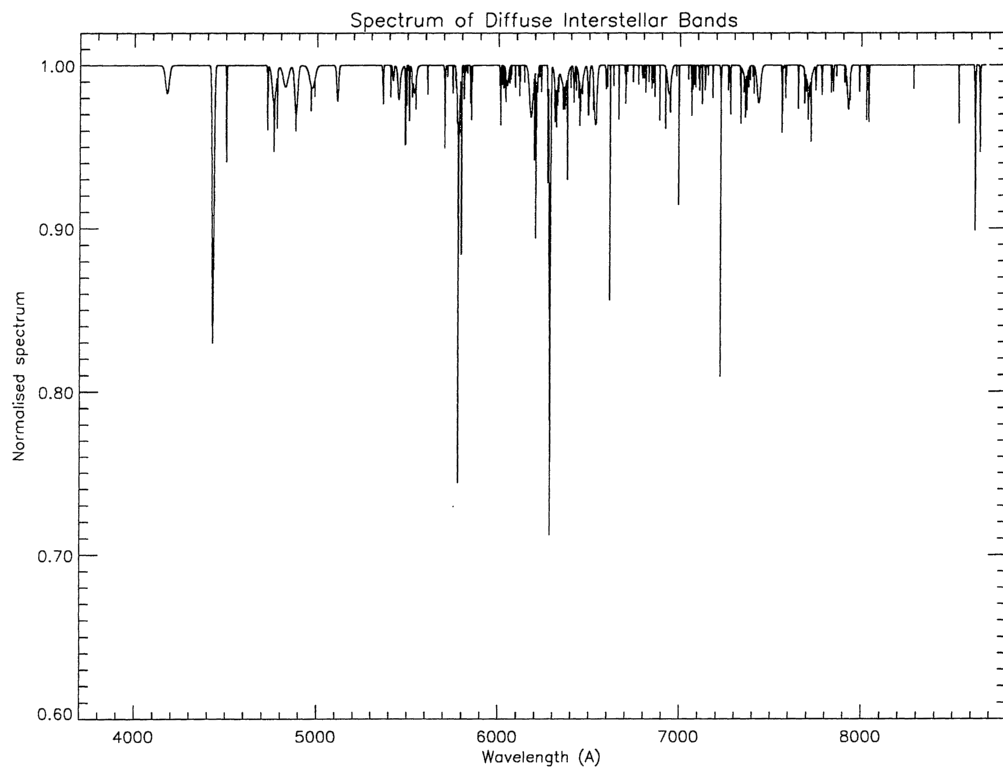


Figure 1. Diffuse interstellar band spectrum reported in Ref. [33]. Credit: P. Jenniskens and F.-X. Désert, *A&A*, 106, 47, 1994, reproduced with permission ESO.

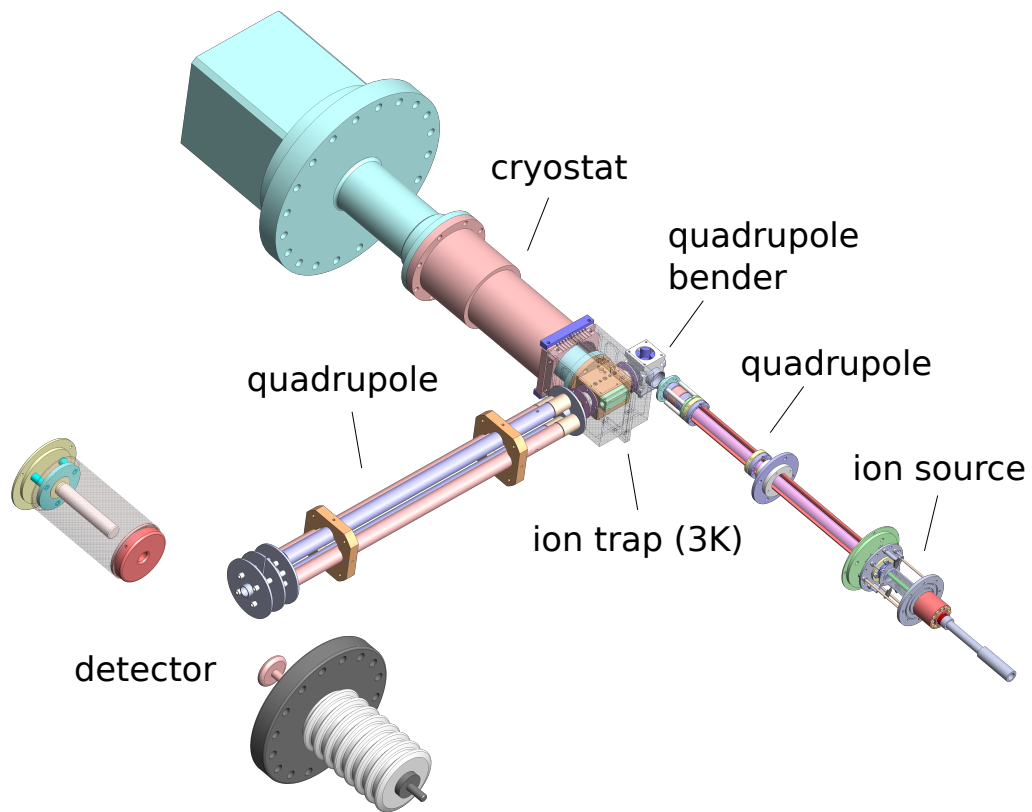


Figure 2. The cryogenic ion trapping instrument consists of several modules contained within a series of high vacuum chambers. Ions generated in the source chamber are mass-selected using a quadrupole, turned through 90° and injected into the cryogenic trap. Here the ions are confined in the radial direction using an inhomogeneous RF field and in the axial direction by two cylindrical electrodes. The trap is mounted onto the second stage of a closed cycle helium cryostat, and the temperature of the walls can be varied from 3 to 300 K. After interaction with laser radiation the trap contents are analyzed using a quadrupole mass-spectrometer and a Daly detector. Adapted from Ref. [37].

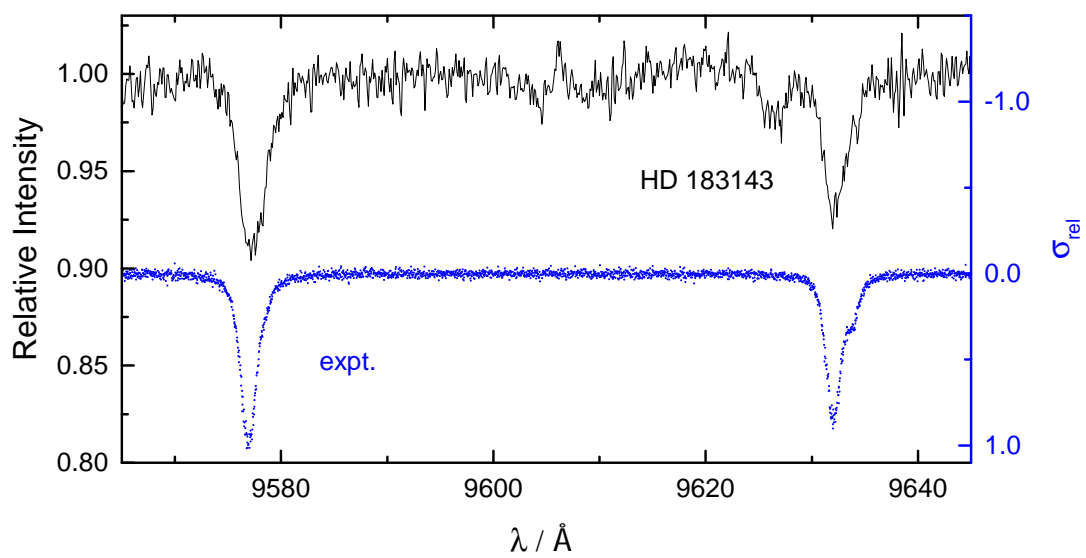


Figure 3. Diffuse interstellar bands observed toward HD 183143 by Foing and Ehrenfreund (black) [74, 102] and the C_{60}^+ spectrum (bottom) inferred from measurements on $C_{60}^+ - He_n$ in a cryogenic trap (blue). Adapted from Ref. 54 where more details are described.

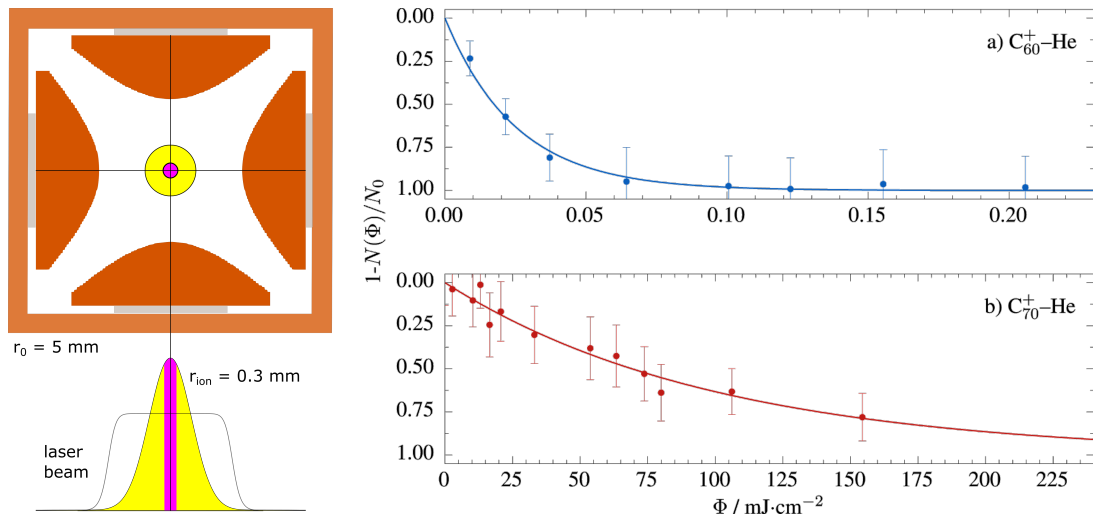


Figure 4. (Left) Sketch of the linear quadrupole ion trap. The four electrodes (orange) are attached to the cold housing using thin sapphire plates (grey). The ion cloud (pink) is constrained to ensure overlap with laser radiation which is transmitted through the trap as a Gaussian beam or with a flat top profile. (Right) Fragmentation of (a) C_{60}^+ - He and (b) C_{70}^+ - He as a function of laser fluence at the wavelengths of the origin bands in their electronic spectra. Exponential fits (lines) to the experimental data (circles) provide information on the cross-sections. Adapted from Ref. [39], where more details are described.

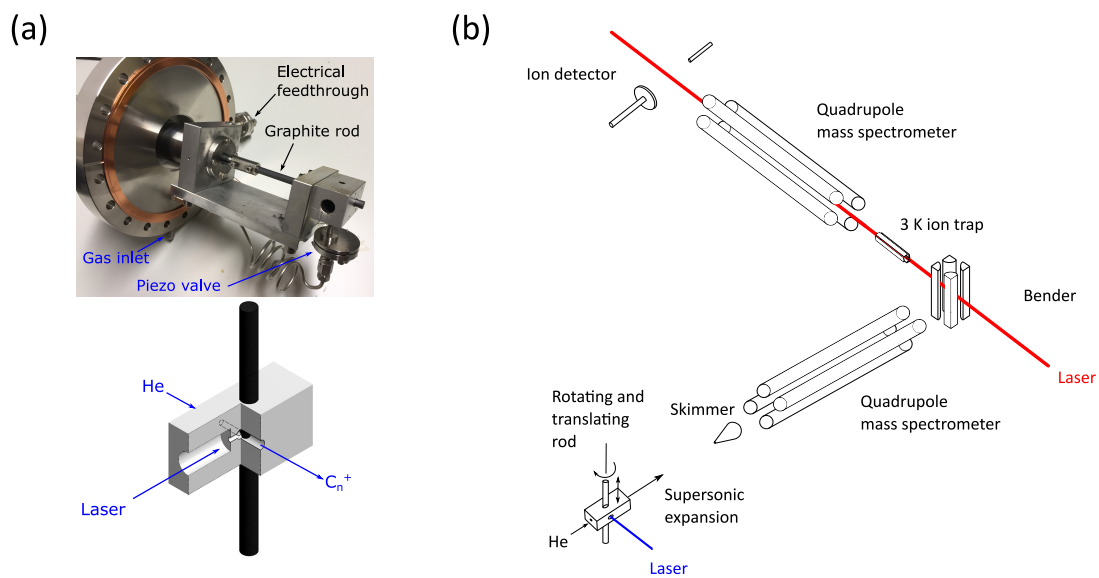


Figure 5. (a) Photograph of the home-built laser vaporization module (top) and schematic of the source block (bottom). (b) Sketch of the apparatus combining laser vaporization synthesis with ion storage at cryogenic temperatures. Molecular ions produced in the source undergo free jet expansion, are mass-selected and then injected into the trap. Here they are accumulated, cooled and subjected to laser radiation before the trap contents are extracted and analyzed by a quadrupole mass spectrometer and a Daly detector. Adapted from Ref. 97.

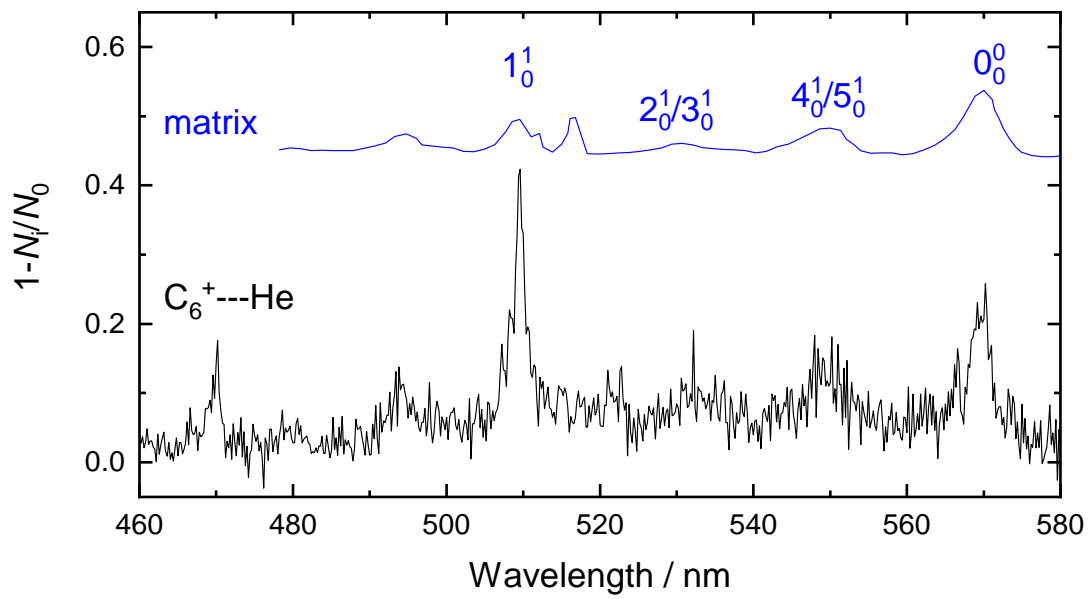


Figure 6. C_6^+ – He photofragmentation spectrum (black) recorded by monitoring the attenuation of ions with $m/z = 76$. Assignment to the ${}^2B_2 \leftarrow X^2A_1$ transition of $c\text{-}C_6^+$ is based on the proximity of these wavelengths to those observed in a 6 K neon matrix (blue). Adapted from Ref. [97]

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