LV-DIB-s4PT: A new tool for astrochemistry

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ABSTRACT

The combination of a 3 K cryogenic radiofrequency ion trapping apparatus and a laser vaporization source is described. This instrument was constructed for the synthesis and characterization of gas phase molecules, particularly those that are difficult to make using traditional organic chemistry routes. The flexible time scale for storage and relaxation afforded by the trap enables spectroscopic investigation of ions that are challenging to cool using supersonic expansions. Routine *in situ* tagging of cations with helium facilitates one-photon experiments. The potential of this instrument is demonstrated by providing data on the $^2B_2 \leftarrow X\ ^2A_1$ electronic transition of cyclic C_6^+, a system that had thus far evaded spectroscopic interrogation in the gas phase.

I. INTRODUCTION

Recent developments in the spectroscopic probing of cold molecular ions have led to advances in fields ranging from biochemistry,[1] catalysis,[2] and astronomy[3] to fundamental molecular physics.[4] One of the most versatile techniques available, at present, is based on ion storage in a temperature variable radiofrequency (RF) trap. Over the last several years, parallel activities in various research groups have pushed the temperature of these devices to their lowest limits. Routine tagging of virtually any cation with helium atom(s) has led to a relatively straightforward route to obtain gas phase spectroscopic information on buffer gas cooled ions.[5] Moreover, a new sensitive method for detecting the absorption of a photon has emerged.[6]

Electronic excitation of buffer gas cooled N_2^+ ($A\ ^2\Pi_u \leftarrow X\ ^2\Sigma_g^+$) stored in a 5 K 22-pole ion trap was used to suppress the formation of N_2^+ – He occurring *in situ* through ternary association. This demonstrated a new approach in ion spectroscopy, termed Laser Induced Inhibition of Complex Growth (LIICG),[6] which has subsequently been exploited in the infrared.[7] Notable successes include the measurement of H_3^+ infrared lines by Gerlich and colleagues[7] and CH_5^+ by Asvany *et al.*, both using a 22-pole trap.[8] In the case of much larger molecular ions, the attachment of a helium atom may only weakly perturb the system, and because one photon excitation readily leads to dissociation by loss of the helium atom over a wide range of wavelengths, spectral information can be obtained in a rather straightforward way. Through such an experimental procedure, the $A\ ^2E_{1g} \leftarrow X\ ^2A_{1u}$ electronic system of C_{60}^+ was shown to be responsible for several diffuse interstellar bands (DIBs).[3]

Advances have also been made using other trap geometries. For example, the wire quadrupole constructed by Jašík *et al.*[9] enabled the ion cloud in the storage device to be constrained to ~0.5 mm diameter, facilitating the measurement of infrared absorption cross sections of benzene dication isomers using commercially available radiation sources.[10] A linear quadrupole ion trap was judged to be appropriate to obtain accurate absolute cross sections for electronic excitation of C_{60}^+, a prerequisite to the determination of its abundance in interstellar clouds.[11] For heavy ions such as these stored in helium, temperatures below 20 K are expected, even in a quadrupole trap due to the favorable mass ratio.[12]

In addition to their unique sensitivity for detecting the absorption of a photon, trapping instruments are attractive for measurements relating to a wide range of applications because they can exploit the suite of ion sources developed by mass spectrometrists. Complex molecules that are difficult to produce using traditional organic chemistry routes can be synthesized and mass selected prior to injection into the trap for spectroscopic and/or chemical probing.

In this context, one relevant and noteworthy production method was pioneered in the laboratory of Smalley in the 1980s and led to the discovery of the fullerenes, paving the way to the active field of nanoscience.

Laser vaporization and cooling in a supersonic expansion has since been used for spectroscopic characterization of a range of organic and metal-containing species (see, for example, Ref. 13 and references therein). However, for large molecular ions containing many internal degrees of freedom, the limited number of collisions in the expansion presents challenges in terms of relaxation of all modes. On the other hand, with buffer gas cooling in a radiofrequency trap, millions of collisions with cold (<5 K) helium atoms are possible in the typical ms–s storage time, resulting in the production of internally cold ions.

The spectacular 1985 mass spectrometry experiments using a graphite disc that led to the discovery of the beautiful fullerene cage structures were carried out with the aim of recreating, in the laboratory, the conditions which could give rise to the formation of carbon chains in environments such as those found in the atmospheres of carbon rich stars.[14] Due to the stability of the identified C_{60} structure, its relevance to the diffuse interstellar band enigma was considered.[14] The relatively recent identification of C_{60}^+ as a DIB carrier[3,15,16] confirmed a 1987 prediction[17] on the astrochemical importance of this cation and has renewed long-held interest in the electronic spectra of other fullerenes and analogs. In this contribution, the combination of a variable temperature radiofrequency ion trapping instrument with a laser vaporization source is described. This was constructed for the purpose of spectroscopic investigation of carbonaceous molecules, particularly those of astrochemical interest. Due to the known facile formation of metal-containing fullerene analogs by laser vaporization, this instrument could be used to obtain gas phase data on the structures long proposed to be of particular interest to the diffuse interstellar band enigma.[18]

The homebuilt apparatus is given the acronym LV-DIB-s4PT, which stands for the laser vaporization-diffuse interstellar band-solid quadrupole trap. To demonstrate its use, gas phase spectroscopic results on the small carbon molecular ion C_6^+ are presented. This system was chosen because the wavelengths of the electronic transitions of both linear and cyclic isomers are known from previous measurements in a 6 K neon matrix.[19] Section II describes the experimental apparatus, while the proof-of-principle results are presented in Sec. III.

II. EXPERIMENTAL

A. Laser vaporization source

A 6.35 mm diameter graphite rod is simultaneously rotated and translated through a metal block similar to that described in Ref. 20. The rod has a clearance of just ~0.1 mm from the metal surface. A cylindrical channel with a diameter of 2 mm is used to admit the helium gas from a pulsed piezovalve based on the design of Gerlich and colleagues.[21] A perpendicular 2 mm channel enables focused laser radiation to strike the graphite rod. The ions exit the source block through a 4 mm diameter channel with 8.5 mm length that is aligned parallel to the helium inlet channel. A schematic view of the housing block is shown in Fig. 1. The design is based on the pulsed laser vaporization cluster ion source, sample holder, and source assembly developed by Duncan.[13]

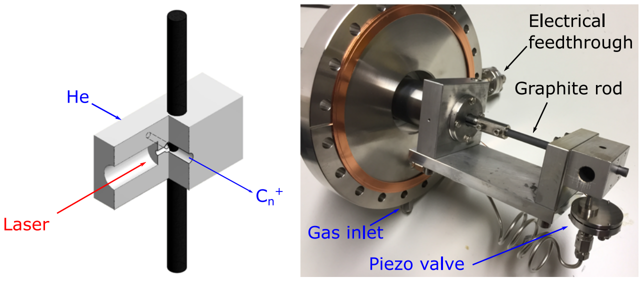

FIG. 1. Cut away view of the block used in the laser vaporization source (left) and photograph of the source assembly (right). The helium is introduced by a piezovalve connected to the inlet channel using a thin piece of Teflon, and an orthogonal 2 mm channel is used to admit the focused laser radiation.

The species produced in the source block undergo free jet expansion in a high vacuum chamber evacuated by a single turbomolecular pump with a N_2 pumping speed of 685 l/s. The entire assembly of the source, including the rotating/translating system, gas inlet, piezovalve, and electrical feedthrough is mounted onto a single ConFlat-160 flange, facilitating easy removal for cleaning and replacement of the graphite rod. The resulting supersonic expansion of the neutral plasma is collimated by a commercial skimmer with a 2 mm diameter orifice. This is mounted onto a differential wall separating the source chamber from the first quadrupole mass spectrometer of the DIB-s4PT apparatus (see Sec. II B). The skimmer orifice is located ~25 cm downstream from the nozzle, and this distance can be easily varied by adaptation of the source vacuum chamber in this modular instrument.

With the current setup and operating the piezovalve and laser at 10 Hz, several thousands of ions of virtually any multiple (1–100) of 12 amu can be observed at the Daly detector. At this repetition rate, pulsing the voltage applied to the piezovalve from −150 V to +150 V for 30 μs causes the pressure in the source chamber to rise from 10^{-9} mbar to a maximum of 10^{-5} mbar. By varying the voltage applied to the piezovalve, the time delay between the laser and gas pulse, and the laser fluence, changes to the distribution of C_n^+ result. This includes the observation of the pattern of peaks separated by 24 amu, which is characteristic of the formation of fullerenes. Such well known effects are thoroughly documented in the literature (see, for example, Ref. 22 and references therein) and are not repeated here.

B. Ion trapping instrument

The central part of the ion trapping machine is described in Ref. 11. Following the synthesis in the laser vaporization source, the resulting cations enter the DIB-s4PT instrument through a skimmer. A sketch of the geometry is shown in Fig. 2. Note that the electrostatic electrodes located between the RF devices have been omitted for clarity. The first quadrupole mass spectrometer has length, $l = 20$ cm, and rod diameter, $d = 9.5$ mm, operates at a frequency of 1.2 MHz and allows mass selection (or transmission) of ions with m/z up to 2000 amu. The ion beam exiting the quadrupole is turned

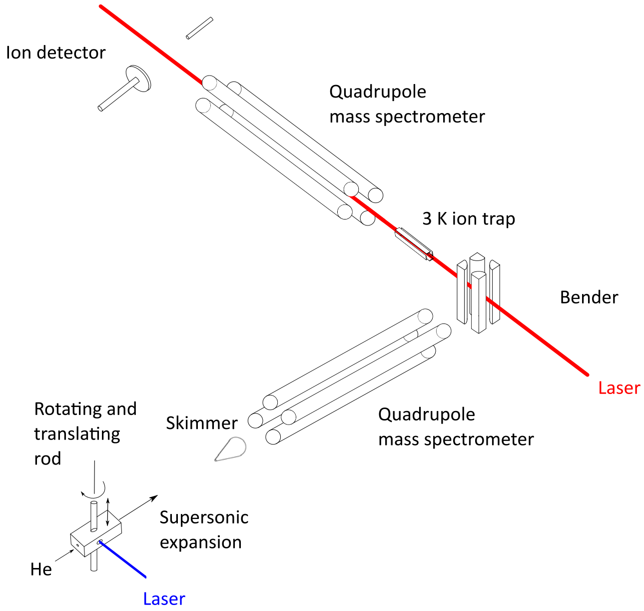

FIG. 2. Sketch of the LV-DIB-s4PT instrument. The assembly is modular and housed within a series of high vacuum chambers. A neutral plasma generated in the source undergoes free jet expansion in the source chamber and is collimated using a skimmer. Ions are mass selected using a quadrupole mass spectrometer, turned through 90° by an electrostatic bender and injected into the ion trap. Following cooling and spectroscopic probing, the contents are extracted, analyzed using a quadrupole mass spectrometer and detected with a Daly detector.

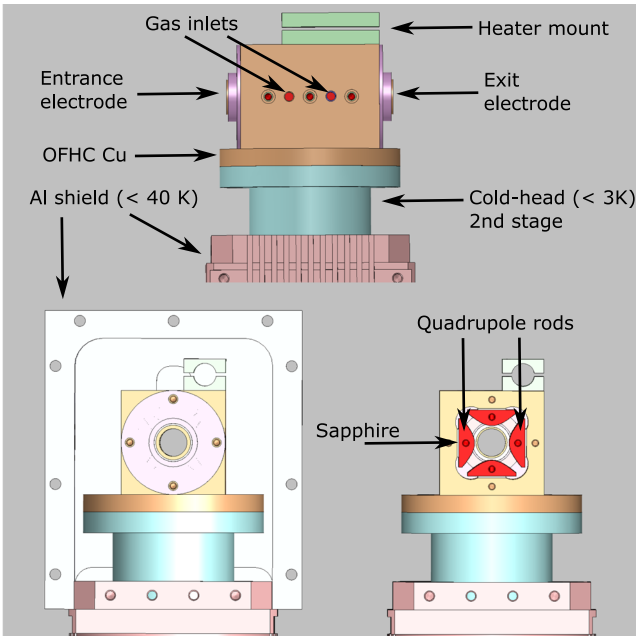

FIG. 3. Solid quadrupole trap (s4PT). The copper housing block is mounted onto the 2nd stage of the cold-head using four M5 screws (not shown). It is surrounded by an aluminum shield that consists of two halves (bottom left, one half not shown). The ions are confined in the axial direction by the entrance and exit electrodes that are mounted onto the copper block (top and bottom left). The entrance electrode has been omitted from the drawing on the bottom right to enable visualization of the four quadrupole rods.

through 90° using an electrostatic quadrupole bender and injected into a linear quadrupole ion trap that is mounted onto the second-stage of a closed cycle helium cryostat. The trap walls reach temperatures as low as 2.6 K, and this can be varied by the use of a cartridge heater mounted onto the copper block housing of the RF device.

This solid quadrupole trap[11] is shown in Fig. 3. The housing was machined from a single piece of oxygen-free copper and is mounted onto the 2nd stage of the cold-head (Sumitomo RDK 205E). Thin sapphire plates isolate the quadrupole rods from the housing block. The trap is surrounded by an aluminum shield that is attached to the 1st stage of the cold-head, reaching temperatures below 40 K. In the trap, the ions are cooled through inelastic collisions with the helium buffer gas. The latter is introduced using a piezovalve connected to the trap using a thin piece of Teflon tube that passes through a hole in the aluminum shield and into one of the gas inlets indicated in Fig. 3. For cooling heavy ions, the piezovalve is resonantly excited for several hundred milliseconds. Number densities of 10^{15}–10^{16} cm^{-3} are readily achieved, and absolute pressures are monitored with a baratron. Another thin piece of Teflon tube extends from one of the shown gas inlets through a hole in the aluminum shield, where it joins a 1/8″ stainless steel tube connected to the baratron. In typical experiments, the buffer gas is pumped out for several hundred milliseconds prior to ion extraction. The ions are confined in the axial direction by the indicated cylindrical entrance and exit electrodes. The voltages applied to these are pulsed to allow injection and extraction, respectively. Before ejection, the ions are probed using tunable radiation, with either pulsed or continuous wave sources. The trap contents are analyzed using a quadrupole mass spectrometer of length, l = 20 cm, with rod diameter d = 9.5 mm operating at frequency of 1.2 MHz and detected using a traditional Daly-type ion detector. With this apparatus, it has been demonstrated that ions with absorption cross sections of 10^{-19} cm^2 are easily observable.[11]

III. RESULTS AND DISCUSSION

A. Mass spectra

The laser vaporization source described in Sec. II A is demonstrated as follows. By operating the first quadrupole mass spectrometer in transmission (RF only) mode, an ion beam has been guided through the instrument to the second quadrupole mass spectrometer, allowing mass spectra of ions produced in the source to be recorded. Some typical results are presented in Fig. 4. These were obtained using ∼10 mJ of laser radiation from a pulsed Nd:YAG pumped dye laser (λ = 645 nm) focused using a 20 cm lens and synchronized with the 30 μs gate of the piezovalve. Under these conditions, the mass spectrum indicates the formation of carbon cations C_n^+ with $n = 6$–70.

Mass spectra obtained following the injection of m/z 72 (left) and 120 (right) into the cryogenic trap operating at a nominal temperature, T_{nom} = 3.2 K, are presented in Fig. 5. The timing sequence for the experiment is shown in Fig. 6. The potential of the entrance

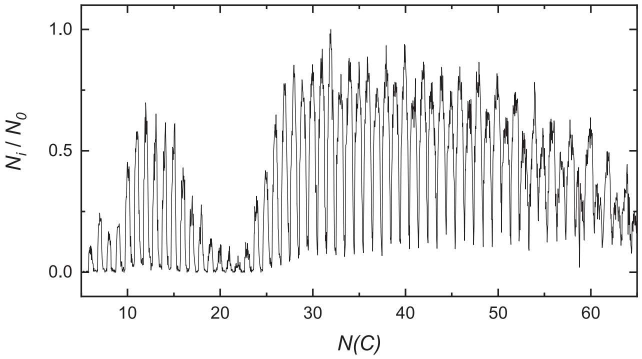

FIG. 4. Mass spectrum recorded using the source outlined in Sec. II A. The number of ions produced from a single source laser pulse was monitored on each mass channel. The normalized data are plotted as a function of the number of carbon atoms, $N(C)$, and were obtained using a 30 μs helium pulse.

electrode is lowered for the first 250 ms, allowing accumulation of ions produced during 3 laser pulses of the 10 Hz source. During the first 500 ms, the stored ions interact with the helium buffer gas that is present at number densities of some 10^{15} cm^{-3}. The buffer gas is then pumped out for several hundred milliseconds before the ion cloud is extracted by lowering the potential of the exit electrode. The trap contents are then analyzed with a quadrupole mass spectrometer. In these experiments, the RF voltage applied to the quadrupole rods of the trap is switched off prior to the beginning of the next trapping cycle to ensure that all ions are removed from the trap. The ion storage process is repeated at a rate of 1 Hz.

As shown in Fig. 5, under these conditions a significant fraction of primary C_n^+ ions can be converted into $C_n^+ - He_n$ complexes. The presented mass spectra indicate the formation of $C_6^+ - He_n$ with $n = 1$–3 and $C_{10}^+ - He_n$ with $n = 1, 2$. For spectroscopic measurements, it is usually advantageous to maximize the number of ions appearing on the $n = 1$ mass channel, through adjustment of helium number density, interaction time, and temperature. A nice discussion of tagging fullerene ions with helium in a wire quadrupole trap has been reported by Gerlich *et al.*[23]

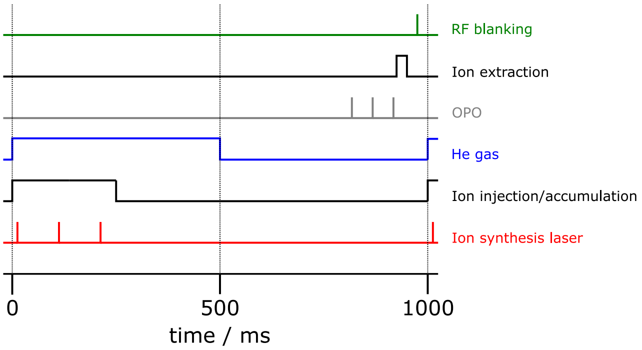

FIG. 6. Timing sequence. The potential of the entrance electrode is lowered for 250 ms to enable accumulation of mass-selected ions obtained from 3 source laser pulses. In the trap, the ions interact with helium during the first 500 ms of the timing sequence. After pumping out the buffer gas, the ion cloud is exposed to radiation from a pulsed OPO prior to analysis using a quadrupole mass spectrometer. A mechanical shutter controls the number of OPO pulses the ion cloud is exposed to. The trap RF voltage is switched off before the beginning of the next trapping cycle to ensure that all ions are removed.

B. Spectroscopic measurements

Mass selection of m/z 72 using the first quadrupole enabled injection of C_6^+ into the cryogenic ion trap. Through the interaction between the stored ions with helium buffer gas, present at number densities of some 10^{15} cm^{-3}, $C_6^+ - He$ are readily produced. After pumping out the He for several hundred milliseconds, the stored ion cloud is exposed to pulsed radiation provided by a tunable optical parametric oscillator (OPO) (5 cm^{-1} bandwidth). The timing sequence for the measurement is shown in Fig. 6. The $C_6^+ - He$ ions are exposed to 3 pulses from the OPO prior to ion extraction. The number of ions with m/z 76 are monitored on alternate trapping cycles with (N_i) and without (N_0) radiation, respectively, to account for long term fluctuations in the ion beam. One-photon fragmentation spectra of $C_6^+ - He$ are recorded by monitoring the attenuation ($1 - N_i/N_0$) of ions with m/z 76 as a function of OPO wavelength.

Cyclic C_6^+ is an open shell system possessing a $^2A_1$ ground electronic state in C_{2v} symmetry. According to theory,[24] this species has

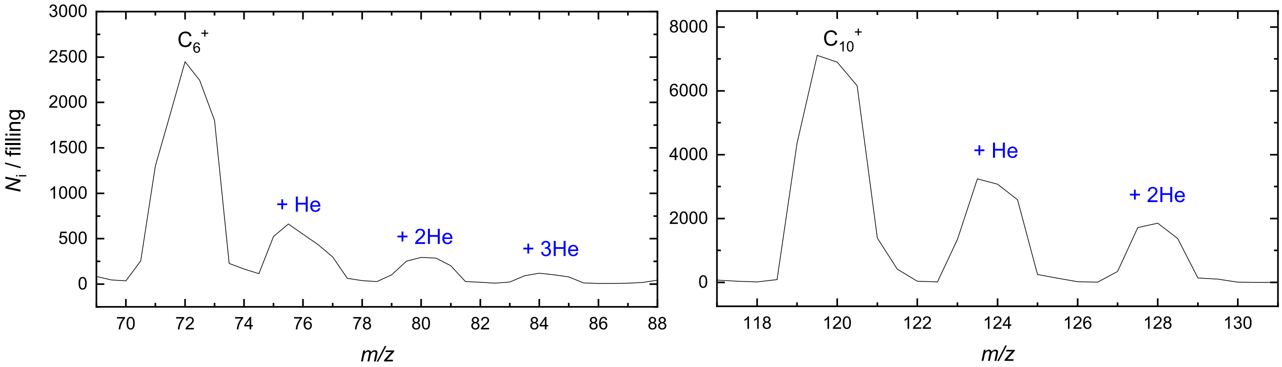

FIG. 5. Typical mass spectra obtained after storage of mass-selected C_n^+ ions in a cold (T_{nom} = 3.2 K) and dense (10^{15} cm^{-3}) helium buffer gas. The left panel shows the formation of weakly bound helium complexes with C_6^+ and the right panel with C_{10}^+. See the text for a discussion.

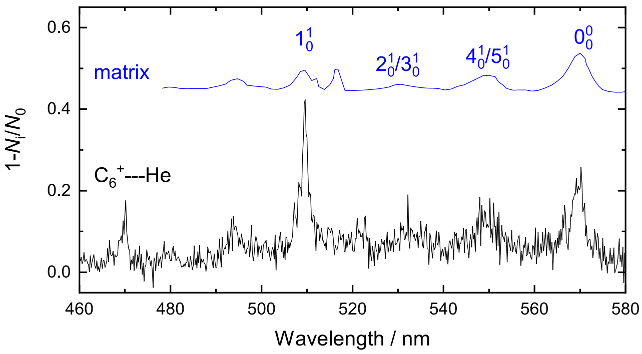

FIG. 7. $C_6^+ - He$ photofragmentation spectrum (black) recorded by monitoring the attenuation of ions with m/z = 76. The labels indicate assignment to the $^2B_2 \leftarrow X\ ^2A_1$ transition of $c - C_6^+$ based on the proximity of these wavelengths to those observed in a 6 K neon matrix (blue). The top spectrum is a digitized version of that presented in Ref. 19.

an allowed electronic transition to the (2) $^2B_2$ excited state at around 400 nm with an oscillator strength, $f = 0.03$. Electronic transitions associated with this C_6^+ isomer have been reported previously following measurements in a 6 K neon matrix.[19] In these experiments, cyclic C_6^+ was generated in a hot cathode discharge source from perchlorobenzene or perbromobenzene precursors. Based on the proximity of the observed $C_6^+ - He$ absorption wavelengths shown in Fig. 7 with those attributed to $c - C_6^+$ in a neon matrix, it can be concluded that this structure is produced under the conditions used in our source. By increasing the fluence of radiation at the wavelength of the origin band near 570 nm, a maximum attenuation of $C_6^+ - He$ ions of 0.5 is observed. A possible reason is that more than one C_6^+ isomer is produced in the laser vaporization synthesis. Preliminary results with a dye laser show a weak absorption at around 655 nm, broadly consistent with the expected wavelength of the $^2\Pi_g \leftarrow X\ ^2\Pi_u$ electronic transition of $l - C_6^+$ observed by Maier and coworkers.[19] This will be explored in future experiments.

The proof-of-principle results presented here demonstrate that this instrument can be used to obtain spectroscopic information on a whole range of structures that contain only carbon atoms and for which there exists little or no experimental data. For example, to the best of our knowledge, gas phase electronic spectra of cations have been reported for just C_2^+, C_{60}^+, C_{70}^+, and C_{70}^{2+}.[3,11,25,26] The determination of accurate gas phase wavelengths, which can be readily obtained through a variety of action spectroscopy approaches including helium tagging, LIICG or photofragmentation, as well as the measurement of absorption cross sections, will enable assessment of their detectability in interstellar environments.

IV. CONCLUSION

The results of proof-of-principle spectroscopic experiments on C_6^+ were presented. Gas phase data on this small carbon cation, generated by laser vaporization of a graphite rod, were obtained by one-photon dissociation of weakly bound $C_6^+ - He$ complexes synthesized in a 3 K ion trap. Its electronic transition was observed in the visible and the presented measurements point to the formation of more than one structural isomer of C_6^+ in the source. It is anticipated that the described LV-DIB-s4PT instrument, which combines nonstandard methods for the synthesis and characterization of molecular ions, will enable spectroscopic investigation of species of astrochemical interest that have evaded detection by more traditional approaches.

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