Spectroscopic characterization of C\textsubscript{7}H\textsubscript{3}\textsuperscript{+} and C\textsubscript{7}H\textsubscript{3}\textsuperscript{*}: electronic absorption and fluorescence in 6 K neon matrices†

Arghya Chakraborty, Jan Fulara, Rainer Dietsche and John P. Maier*

Mass selective deposition of C\textsubscript{7}H\textsubscript{3}\textsuperscript{+} (m/z = 87) into solid neon reveals the 1 \textsuperscript{3}A\textsubscript{1} ← X \textsuperscript{1}A\textsubscript{1} electronic absorption system of hepta-1,2,3,4,5,6-heptahexaenyl cation B\textsuperscript{*} [H\textsubscript{2}CCCCCCCCH\textsuperscript{+}]\textsuperscript{+} with an origin band at 441.3 nm, 1 \textsuperscript{3}A\textsubscript{1} ← X \textsuperscript{1}A\textsubscript{1} transition of 2,4-pentadiynyl-1-ethynyl cation C\textsuperscript{*} [HCCCHCCCCH\textsuperscript{+}]\textsuperscript{+} starting at 414.6 nm and the 1 \textsuperscript{3}A\textsubscript{1} ← X \textsuperscript{1}A\textsubscript{1} one of cyclopropenylium,1,3-butadiynyl cation A\textsuperscript{*} [HCCCCC<\text{CH=CH}\text{H}]\textsuperscript{+} with an onset at 322.2 nm. Vibrationally resolved fluorescence was observed for isomer B\textsuperscript{*} upon laser excitation of the absorption bands in the 1 \textsuperscript{3}A\textsubscript{1} ← X \textsuperscript{1}A\textsubscript{1} transition. After neutralization of the cations in the matrix five absorption systems of the C\textsubscript{7}H\textsubscript{3} neutral radicals starting at 530.3, 479.4, 482.3, 325.0 and 302.5 nm were detected. These were identified as the 1 \textsuperscript{3}A\textsubscript{1} ← X \textsuperscript{2}A\textsubscript{1} and 2 \textsuperscript{3}A\textsubscript{2} ← X \textsuperscript{2}A\textsubscript{2} electronic transitions of 2-(buta-1,3-diynyl)cycloprop-2yl-1-1ylidene E\textsuperscript{*} [HCCCCC<\text{CH=CH}\text{H}]\textsuperscript{+}, 1 \textsuperscript{2}B\textsubscript{1} ← X \textsuperscript{2}B\textsubscript{1} of 1,2,3,4,5,6-heptahexaenyl B\textsuperscript{*} [H\textsubscript{2}CCCCCCCCH\textsuperscript{+}], 3 \textsuperscript{2}B\textsubscript{1} ← X \textsuperscript{2}B\textsubscript{1} of 3-buta-1,3-diynyl-cyclopropenyl \textsuperscript{A}\textsuperscript{*} [HCCCC<\text{CH=CH}\text{H}]\textsuperscript{+} and 2 \textsuperscript{3}B\textsubscript{1} ← X \textsuperscript{3}B\textsubscript{1} transition of 1,2-divinylidene-cyclopropenyl radical \textsuperscript{F}\textsuperscript{*} [HCC-cyc-(CCHC)-CCH\textsuperscript{+}], respectively. The assignment is based on calculated vertical excitation energies using the CASPT2 method. Comparison of the calculated harmonic vibrational frequencies with those inferred from the spectra supports the assignment.

1. Introduction

A variety of unsaturated species including polycyclic aromatic systems are produced during combustion of hydrocarbons in an oxygen deficient environment, as established by gas chromatography and molecular beam mass spectroscopy (MBMS).\textsuperscript{1-5} The presence of large aromatic systems in soot starting from small hydrocarbons is not entirely understood. Theoretical kinetics and MBMS suggest that C\textsubscript{2n+1}H\textsubscript{3} systems play a vital role.\textsuperscript{6-9} The recombination mechanism of the propargyl radical, C\textsubscript{3}H\textsubscript{3}\textsuperscript{*}, is considered as one of the key processes in the formation of larger aromatics.\textsuperscript{10-12} Thus the C\textsubscript{2n+1}H\textsubscript{3}\textsuperscript{*} class of molecules presents an intriguing subject for a spectroscopic exploration, and the identification of the electronic absorptions of the various isomers will enable their in situ monitoring in soot formation.

The propargyl radical has been studied by microwave,\textsuperscript{13} infrared,\textsuperscript{14,15} photoelectron\textsuperscript{16} and electronic\textsuperscript{17,18} spectroscopy techniques. The propargyl cation has also been characterized by electronic and infrared spectroscopy.\textsuperscript{19,20} The next member of this series, the C\textsubscript{2n}H\textsubscript{3}\textsuperscript{*} radical, has been proposed as a reactive intermediate in the photodissociation of benzene.\textsuperscript{21} It can be produced in fuel rich flames and plays a role in the formation of polycyclic aromatic hydrocarbons.\textsuperscript{8,21,22} In fact, the peak of C\textsubscript{2n}H\textsubscript{3}\textsuperscript{+} with m/z = 63 is often found in the mass spectra of hydrocarbons. There is only circumstantial experimental and computational understanding on C\textsubscript{2n}H\textsubscript{3}\textsuperscript{+} and C\textsubscript{2n}H\textsubscript{3}\textsuperscript{*} isomers except for one electronic spectrum recorded in the gas phase by a resonant two-color-two-photon-ionization (R2C2PI) technique.\textsuperscript{23}

Interstellar clouds contain a rich collection of exotic molecular systems because of the very low density and temperature. In the laboratory, unstable organic systems like carbon chains, combined with cyclic rings and with heteroatoms, have been studied by microwave spectroscopy.\textsuperscript{24-26} The C\textsubscript{2n}H\textsubscript{3}\textsuperscript{*} and C\textsubscript{2n}H\textsubscript{3}\textsuperscript{+} species may also be relevant in the planetary atmosphere of Titan.\textsuperscript{27}

The present study focuses on the characterization of C\textsubscript{2n}H\textsubscript{3}\textsuperscript{+} and C\textsubscript{2n}H\textsubscript{3}\textsuperscript{*} species isolated in neon matrices at 6 K by electronic spectroscopy. C\textsubscript{2n}H\textsubscript{3}\textsuperscript{+} or C\textsubscript{2n}H\textsubscript{3}\textsuperscript{−} are produced using ion sources, then mass selected and subsequently neutralized. On the basis of the electronic excitation energies obtained by CASPT2 calculations after ground state optimization of the possible isomers, the assignments of the observed absorptions have been made.

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4cp00043a
2. Experimental

The approach used combines mass spectrometry with the matrix isolation technique. Ions are generated in a hot-cathode discharge source from diverse organic vapors and extracted through electrostatic lenses. The ion beam is then led into a quadrupole filter for mass selection. Subsequently, the ions are co-deposited with excess of neon, including traces (1:20 000) of chloromethane (CH3Cl), on a rhodium coated sapphire substrate held at 6 K. CH3Cl is added to diminish the space charge during growth of the matrix and to suppress neutralization of the cations. It captures electrons released from the metal surface near the matrix by the impinging of cations with an energy of ~50 eV. The Cl− anions, formed by dissociative electron attachment to CH3Cl, balance the charge. The matrix is grown to a thickness of 100–150 µm.

The spectra are recorded in the 250–1100 nm range in a “waveguide” manner. The detection system consists of a 0.3 m spectrograph equipped with three rotatable gratings and two wavelength specific CCD cameras. Light after passing through the 20 mm length of the matrix, parallel to the substrate surface, is collected by a lens onto a bundle of quartz fibers and into the spectrograph, wavelength dispersed, and recorded using a CCD camera. Halogen and a high pressure xenon arc lamp are the two light sources used.

The species trapped in neon were excited at an incident angle of ~45° to the cold substrate surface with a pulsed, tunable laser of bandwidth of ~3 cm−1 and an energy of 2–30 mJ. The emission was collected perpendicular to the matrix surface and 45° to the laser beam. The light collected by the optical fibers was transferred to the spectrograph, dispersed, and recorded using a CCD camera, as for the absorption measurements. The measurements were started at ~2 nm longer wavelength than the excitation one to avoid saturation of the camera by the scattered laser light.

The cations and anions with m/z = 87 were produced using different ion sources. Toluene was used as a precursor of C7H3+, while C7H3+ was generated from a 1:1 mixture of diacetylene and propyne. Indene is a rich source for C7H5+ ions and m/z = 89, C7H5+, is the strongest peak after the parent ion in the mass spectrum of C6H8.

3. Results and discussion

3.1 Absorption

Strong absorptions are found in the 300–450 nm range (Fig. 1) along with some weaker ones between 470 and 540 nm after deposition of mass selected C7H3+ in a neon matrix containing CH3Cl. The strongest narrow band is seen at 441.3 nm and that of a broader peak at 414.6 nm (Fig. 1, black trace). In addition, a system with an onset at 322.2 nm is apparent. To distinguish absorptions of the cations from neutrals, the matrix was exposed to λ > 260 nm photons from a medium pressure mercury lamp. The Cl− anions generated from CH3Cl release electrons which recombine with C7H3+ producing neutral species. The intensity of the absorption systems commencing at 441.3,
303 nm system lies close to the onset of the 2-(buta-1,3-diylnyl)cycloprop-2yl-1-ylidene radical (isomer E* in Chart 1) absorption, identified at 528.3 nm in the gas-phase\textsuperscript{23} and the pattern of the vibrational progression is similar.

The enhancement of isomer E* absorption with higher kinetic energy deposition, as well as in C\textsubscript{7}H\textsubscript{5} anion deposition at even higher kinetic energy \(|\sim 150\) eV, reveals that E* is produced as a secondary product during matrix growth. The primary ions should have a similar structure as E* – a cyclic three-membered carbon ring with a butynyl group C\textsubscript{4}H attached. The E* isomer and the corresponding primary cation differ only in the position of hydrogen atoms. Stronger absorption of l-HC\textsubscript{7}H\textsuperscript{+} seen in the spectra obtained with higher than 50 eV deposition energy suggests that the other primary C\textsubscript{7}H\textsubscript{5}\textsuperscript{+} cations have an open chain structure, for which the removal of a hydrogen atom is facile and leads to the enhancement of the l-HC\textsubscript{7}H\textsuperscript{+} absorptions. Though the identification of the secondary products of C\textsubscript{7}H\textsubscript{5}\textsuperscript{+} produced under higher kinetic energy conditions provide a hint about the structure of the primary cations, the information derived from the spectra is not sufficient to assign the

![Figure 2](image-url) Section of the absorption spectra recorded: after deposition of C\textsubscript{7}H\textsubscript{3}\textsuperscript{+} with \(|\sim 50\) eV deposition energy (black), after 30 min irradiation by a medium pressure mercury lamp \(|\lambda > 260\) nm (green), after deposition of C\textsubscript{7}H\textsubscript{3}\textsuperscript{+} cations with kinetic energy \(|\sim 90\) eV (blue) and after depositing C\textsubscript{7}H\textsubscript{3}\textsuperscript{-} followed by irradiation (pink).

![Chart 1](chart-url) Structure and relative ground state energy (kJ mol\textsuperscript{-1}) of the five isomers of C\textsubscript{7}H\textsubscript{3}\textsuperscript{+} and C\textsubscript{7}H\textsubscript{5}\textsuperscript{+} calculated using DFT (bold) and the MP2 level of theory (italic) using the cc-pVDZ basis set. The corresponding C\textsubscript{7}H\textsubscript{5}\textsuperscript{-} anions have been optimized by DFT using the aug-cc-pVDZ basis set. Bond lengths (\textgreek{\AA}) given correspond to the cations optimized by the MP2 method.
observed absorptions to specific species. Theoretical studies on the stability of different isomers of C$_7$H$_3$ and the corresponding neutrals as well as excitation energies of these species are needed and have been carried out (vide infra).

### 3.2 Fluorescence

All the intense absorption bands shown in Fig. 1 were excited with a laser for fluorescence detection after depositing C$_7$H$_3$ with neon. The concentration of the CH$_3$Cl scavenger was kept lower (1:50 000) to have enough cations as well as neutrals in the matrix. The neutral systems at 530.3 and 482.3 nm do not fluoresce. However, a structured emission was detected, commencing at 442.7 nm and extending to 514 nm, after laser excitation of the sharp band at 441.3 nm (Fig. 3). The same fluorescence spectrum, though less intense, was obtained when the laser photons matched the wavelengths of weak absorption peaks lying 558, 809 and 1087 cm$^{-1}$ above the 441.3 nm origin. This confirms that these absorption bands belong to the same electronic system. Origin of the fluorescence and absorption overlap at 442.4 nm which is the zero-phonon line (ZPL) of the two spectra. The wavelengths of the fluorescence bands are collected in Table 2. No fluorescence was detected upon excitation of the 414.6 nm and 322.2 nm systems of C$_7$H$_3$ and 325 and 303 nm of neutrals.

### 3.3 Computations: comparison with experiment

Geometry optimization of plausible twelve cations and their neutral isomers (Table S1, ESI†) was carried out by density functional theory (DFT) with the B3LYP functional and the cc-pVDZ basis set using the Gaussian 09 program suite. Harmonic vibrational frequencies in the ground state were calculated to check whether the structures are real minima on the potential energy surface (PES). The geometries of all species were then refined using the Moller–Plesset perturbation (MP2) method using the cc-pVDZ basis set and used as a starting point for excitation energy calculations.

The vertical excitation energies were calculated using a second order multiconfigurational perturbation theory (CASPT2) implemented in the Molcas program package. 13 electrons partitioned in 13 orbitals formed the active space and six roots were calculated for the irreducible representation of each species. The vertical excitation energies obtained are given in Table S2 (ESI†) and compared with the origin band positions in the spectra of C$_7$H$_3$$^+$ and C$_7$H$_3$ in neon matrices. The results for the five lowest energy structures, A*, B, C, F, J, and for isomer E* for which the electronic transition starting at 530.3 nm was already identified in a gas-phase study are discussed in the following paragraphs. The structure of the A, B, C, F, J and E molecules is presented in Chart 1 together with the ground state energies calculated for the cationic, anionic and neutral forms. The bond lengths for the cations, calculated by the MP2 method, are shown. The global minimum on the C$_7$H$_3$$^+$ PES, predicted by both theoretical methods, is isomer A*, a three-membered carbon ring fused with the linear C$_3$H chain. The second lowest energy structure F* has the same three-membered carbon ring motif but with two ethynyl groups attached. The next is energy isomer J* – consisting of fused three and six carbon rings – located 40 kJ mol$^{-1}$ above A* according to MP2 calculations. Isomers B* and C* are almost isoenergetic and lie 61 and 69 kJ mol$^{-1}$ above A*. At the DFT level B* is more stable than J*. Cation E* lies 452 kJ mol$^{-1}$ above the most stable A*. However E* is also focused on because the electronic transition of E* is observed in the present studies. The most stable structure of neutral C$_7$H$_3$ is isomer J*. The relative stability and the energy order of the C$_7$H$_3$$^+$ isomers obtained from the previous DFT calculations using the smaller basis set differ from the present results. The energies obtained from the MP2 calculations are the more reliable. However both DFT and MP2 methods fail to describe properly the electronic systems in the case of near degeneracy. More advanced methods are needed for this purpose.

Isomers A*, A$^+$ and F*. The ground state of the two lowest energy C$_7$H$_3$$^+$ cations, A$^+$ and F$, has X $^1$A$_1$ symmetry. The MS calculations predict two dipole-allowed electronic transitions to the 1 $^1$A$_1$ and 2 $^1$A$_1$ states below 6.5 eV (Table 3). The first 1 $^1$A$_1$ electronic state of A$^+$ and F$^+$ lies at 4.13 and 5.46 eV above the X $^1$A$_1$ state, with oscillator strengths of the transitions 0.40 and 0.13, respectively. The second 2 $^1$A$_1$ ← X $^1$A$_1$ at around 6 eV is two orders of magnitude weaker in intensity. These results are consistent with earlier CASSCF and MRCI calculations on cyclic C$_4$H$_7$ which predict a dipole allowed electronic transition at around 8 eV. Substitution of two hydrogen atoms in c-C$_5$H$_7$ with two ethynyl groups (isomer F$^+$) shifts this transition to 5.46 eV. A much lower energy of 4.13 eV was predicted for A$^+$ where one hydrogen atom of c-C$_5$H$_7$ is replaced with a butynyl group, because the electrons are delocalized over a larger distance.

C$_5$H$_7$, produced from cyclic and acyclic precursors, has been studied in neon matrices. Though its electronic
transition was not observed due to the wavelength being out of the detection range of the setup, the presence of C7H3+ was proven by infrared measurements. One can expect that A+ and F+ are also formed in the present experiments and trapped in the neon matrix, as the conditions were similar to those for C6H4+. However isomer F+, with an electronic transition at around 5.46 eV, could not be observed for technical reasons: the scattering of light from the matrix. The calculations for the neutral F+ predict three electronic transitions from the X 2A2 ground state to the 1 2B1, 2 2B2 and 3 2B2 states at 1.15, 4.44 and 5.64 eV and oscillator strengths of 0.03, 0.04 and 0.19, respectively. These states at 1.15 and 5.64 eV are outside the range of the detection system.

Cation A+, in contrast to F+, has the strong (f = 0.40) 1 1A1 ← X 1A1 transition at lower energy (4.13 eV; 300 nm), close to the 322.3 nm absorption system of C7H3+. In this region, MS-CASPT2 calculations predict also a moderately intense (f = 0.064) 1 2B2 ← X 1A1 transition for isomer J+ (E = 4.30 eV) and a strong one 1 1A1 ← X 1A1 (f = 0.54) for isomer K+ with an energy of 4.36 eV (Table S2, ESI†). Because the oscillator strength of the electronic transition of isomer J+ is an order of magnitude smaller than for the 1 1A1 ← X 1A1 transition of A+ and isomer K+ has an exotic structure and lies much higher in energy on the PES than A+, we therefore assign the 322.3 nm absorption system of C7H3+ to the 1 1A1 ← X 1A1 transition of A+. The calculations overestimate the energy by 0.3 eV. This may be partly because the experimental data are compared with the vertical excitation energy instead with the adiabatic value.

Isomer A+ is likely a progenitor of neutral E+ in the higher kinetic energy deposition experiments, because these two species have the same carbon skeleton (three membered carbon ring with C4H attached) and differ only in the position of two hydrogen atoms. Cations A+ , during hard landing on the matrix surface, possesses enough internal energy to rearrange the two hydrogen atoms.

The section of the electronic spectrum, where the absorptions of A+ are present, is shown in Fig. 4. Three vibrational bands located at 529, 1945 and 2464 cm−1 above the origin belong to this system and correspond to the excitation of the ν0, ν4 modes and their combinations. Harmonic vibrational frequencies in the ground state of A+ calculated at the MP2 level are 538 and 2098 cm−1. The wavelengths of the band maxima of A+ and their assignment are given in Table 1. Two absorption bands of neutral species at 325 and 303 nm are present and likely belong to two different isomers of C7H3+. The calculations predict a moderately intense (f = 0.04) 2 2B1 ← X 2A2 transition of F+ at 4.44 eV and a stronger (f = 0.13) 3 2B2 ← X 2B1 one at 4.76 eV of A+. Other higher energy structures of C7H3+ are excluded from consideration because much weaker electronic transitions for these species are predicted in this region (Table S2, ESI†). The 325 nm system is tentatively assigned to the 2 2B1 ← X 2A2 transition of F+ and the 303 nm absorption to 3 2B1 ← X 2B1 of A+. The calculations overestimate the excitation energy of these transitions by ~ 0.6 eV for both isomers.

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<tr>
<td>487.0</td>
<td>20534</td>
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<tr>
<td>500.0</td>
<td>20000</td>
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<tr>
<td>513.5</td>
<td>19474</td>
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Isomers B+, B+ and C+. The 390–460 nm section of the electronic spectrum measured after deposition of m/z = 8 cations (Fig. 5) shows two absorption systems commencing at 441.3 nm (2.81 eV) and 414.6 nm (2.99 eV) belonging to two C7H3+ isomers. Only four isomers, among all considered structures for which excitation energies were calculated, possess stronger electronic transitions in this region. These are B+, C+, G+ and H+. The two latter higher energy structures can be excluded because they also have even stronger transitions at around 300 nm
Three other excited electronic states of C+ lie 4.2–5.2 eV above X 1A', however the oscillator strengths are two orders of magnitude smaller than the 1 1A' state. The energy of the 1 1A' ← X 1A1 transition of B+ matches with the onset at 441.3 nm (2.81 eV) of the strongest absorption system. Also the origin of the second system at 414.6 nm (2.99 eV) correlates well with the energy of the 1 1A' ← X 1A1 transition of C+. Therefore, the absorptions in the spectrum shown in Fig. 5 are assigned to the 1 1A' ← X 1A1 of isomer B+. and 1 1A' ← X 1A' transitions of C+, respectively. Isomer B+ is a protonated form of l-HC7H+. In the case of the triacetylene cation, addition of one hydrogen atom produces HC6H2+, which has a similar structure as B+. Addition of one hydrogen atom shifts the origin band from 604.2 nm for HC6H+ to 378.6 nm for HC7H2+.36,37 Similarly the absorption of B+ (at 441.3 nm) is shifted ~ 160 nm to blue in comparison to HC7H+ (599.8 nm).30

Table 3  Electronic excitation energies E-cal (eV) and oscillator strength (f) of the dipole allowed electronic transitions for C7H3+ and C7H3 isomers calculated by the MS CASPT2 method and in comparison to the experiment E-exp.

<table>
<thead>
<tr>
<th>Transitions</th>
<th>E-cal</th>
<th>f</th>
<th>E-exp</th>
</tr>
</thead>
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<tr>
<td>A'</td>
<td>X 1A1 → 1 1A1</td>
<td>4.13</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>→ 2 1A1</td>
<td>5.99</td>
<td>0.0050</td>
</tr>
<tr>
<td>A'</td>
<td>X 2B1 ← 1 1A2</td>
<td>1.72</td>
<td>0.0020</td>
</tr>
<tr>
<td></td>
<td>→ 3 1A2</td>
<td>4.76</td>
<td>0.13</td>
</tr>
<tr>
<td>B'</td>
<td>X 1A1 → 1 1A1</td>
<td>2.99</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>→ 2 1A1</td>
<td>3.95</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>→ 3 1A1</td>
<td>4.21</td>
<td>0.0030</td>
</tr>
<tr>
<td></td>
<td>→ 4 1A1</td>
<td>5.53</td>
<td>0.0050</td>
</tr>
<tr>
<td>B'</td>
<td>X 2B1 ← 1 1B1</td>
<td>2.46</td>
<td>0.0020</td>
</tr>
<tr>
<td></td>
<td>→ 2 1B1</td>
<td>5.73</td>
<td>0.0007</td>
</tr>
<tr>
<td>C'</td>
<td>X 1A' → 1 1A'</td>
<td>3.13</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>→ 2 1A'</td>
<td>4.17</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>→ 3 1A'</td>
<td>4.73</td>
<td>0.0008</td>
</tr>
<tr>
<td></td>
<td>→ 4 1A'</td>
<td>5.19</td>
<td>0.040</td>
</tr>
<tr>
<td>C'</td>
<td>X 2A' ← 1 1A''</td>
<td>3.21</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>→ 2 1A''</td>
<td>4.42</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>→ 3 1A''</td>
<td>5.08</td>
<td>0.0080</td>
</tr>
<tr>
<td></td>
<td>→ 4 1A''</td>
<td>5.57</td>
<td>0.020</td>
</tr>
<tr>
<td>E'</td>
<td>X 2A' ← 1 1A'</td>
<td>2.28</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>→ 2 1A'</td>
<td>2.56</td>
<td>0.0020</td>
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<td>→ 3 1A'</td>
<td>3.43</td>
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<td>→ 5 1A'</td>
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<tr>
<td>E'</td>
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<td>0.0002</td>
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<tr>
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<td>→ 2 1A'</td>
<td>2.94</td>
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<tr>
<td></td>
<td>→ 3 1A'</td>
<td>3.1</td>
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<td>3.26</td>
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<tr>
<td>F'</td>
<td>X 1A1 → 1 1A1</td>
<td>5.46</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>→ 2 1A1</td>
<td>6.15</td>
<td>0.0090</td>
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<tr>
<td>F'</td>
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<tr>
<td></td>
<td>→ 2 1B1</td>
<td>4.44</td>
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<tr>
<td></td>
<td>→ 3 1B1</td>
<td>5.67</td>
<td>0.19</td>
</tr>
<tr>
<td>J'</td>
<td>X 1A1 ← 1 1B2</td>
<td>4.30</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td>→ 2 1B2</td>
<td>5.80</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>→ 1 1A1</td>
<td>5.29</td>
<td>0.013</td>
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<tr>
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<td>→ 2 1A1</td>
<td>5.89</td>
<td>0.11</td>
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<tr>
<td>J'</td>
<td>X 2B1 ← 1 1B1</td>
<td>3.36</td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td>→ 2 1B1</td>
<td>4.84</td>
<td>0.074</td>
</tr>
<tr>
<td></td>
<td>→ 3 1B1</td>
<td>6.42</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>→ 3 1A1</td>
<td>3.30</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>→ 4 1B1</td>
<td>5.25</td>
<td>0.063</td>
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</table>

(Table S2, ESI†), in conflict with observations. Isomers B+ and C+ are open chain structures (Chart 1) and are good candidates for the absorptions observed. Both cations, after removal of one hydrogen atom, can readily produce the l-HC7H+ fragment ion as observed in the higher kinetic energy studies. The calculations predict a strong 1 1A' ← X 1A1 transition (f = 0.33) at 2.99 eV and a two orders of magnitude weaker one at 3.95 eV for B'; the first excited 1 1A' state of C+ is 3.13 eV above the X 1A' ground state with an oscillator strength of 0.64.
The vibrational bands present in the absorption and fluorescence spectra of B+ are assigned to specific normal modes using the MP2 calculated, harmonic vibrational frequencies in the ground state of the cation (Table 2). Four totally symmetric a1 modes: \( \nu_4, \nu_6, \nu_5 \) and \( \nu_3 \) are active in the fluorescence spectrum of B+ and only the two former vibrations in the absorption. There is an absorption peak between the \( \nu_9 \) and \( \nu_8 \) bands, 809 cm\(^{-1}\) above the origin, which belongs to B+ because the fluorescence starting at \( \sim 442 \) nm was detected. This band arises from the excitation of two quanta of the \( \nu_{21} \) (b2) mode. In the spectrum of C+ two absorption peaks located at 462 and 725 cm\(^{-1}\) above the origin at 414.6 nm are apparent. The first one is hidden under the l-HC7H+ band. They are attributed to \( \nu_{14} \) and \( \nu_{16} \) mode excitations by comparison with the 472 and 776 cm\(^{-1}\) calculated ground state vibrational frequencies of C+.

As the electronic transitions of B+ and C+ are detected one can expect that B+ and C+ should also be present. A good candidate for these species is the absorption system starting at 482.3 nm (2.57 eV) which gains intensity upon UV irradiation (Fig. 6). The calculations predict a weak \( (f = 0.002) \) 1 \( ^2 \)B1 \( \leftarrow X ^2 \)B1 transition for B+ at 2.46 eV, the 1 \( ^2 \)A2 \( \leftarrow X ^2 \)A2 transition of C+ at 3.21 eV with an oscillator strength of 0.03. Due to a better match of the calculated excitation energy of B+ with the observations, the 482.3 nm system is assigned to its 1 \( ^2 \)B1 \( \leftarrow X ^2 \)B1 transition. Table 1 lists the absorption band maxima and the assignment for the systems of B+, B+, and C+.

**Isomer E+.** The absorption at 530.3 nm shown in Fig. 6 belongs to isomer E+ identified in the gas phase studies at 528.8 nm and assigned to the origin band of the 1 \( ^2 \)A \( \leftarrow X ^2 \)A transition.23 Some unassigned bands at around 481 and 474 nm were also reported. The 474.9 nm absorption system in the neon matrix behaves in a similar fashion to that of 530.3 nm upon irradiation. The calculations predict two transitions 1 \( ^2 \)A \( \leftarrow X ^2 \)A and 2 \( ^2 \)A \( \leftarrow X ^2 \)A at 2.28 and 2.56 eV, with oscillator strengths of 0.01 and 0.002. The computed energies and the intensities agree well with the matrix spectrum with onsets at 530.3 nm (2.34 eV) and 479.5 nm (2.58 eV). Three absorption bands located at 493, 542 and 953 cm\(^{-1}\) above the origin of the first electronic system are assigned to the excitation of the \( \nu_{14}, \nu_{13} \) and \( \nu_6 \) modes on the basis of their proximity to the MP2 calculated ground state vibrational frequencies 508, 587 and 952 cm\(^{-1}\). Table 1 lists the wavelengths of the absorption band maxima and the assignment for isomer E+.

### 4. Concluding remarks

The open chain isomers B+ and C+ and A+ with a three membered carbon ring were identified in the neon matrix after trapping of C7H3+ produced from indene and acyclic precursors. Cation B+ exhibits vibrationally structured fluorescence following excitation into the absorption bands of the 1 \( ^1 \)A1 \( \leftarrow X ^1 \)A1 system. No fluorescence was detected for the isomers A+ and C+. Weak absorptions of neutral C7H3 isomers are also present which gain intensity upon photobleaching of the cations. Increase in intensity of the absorptions of the neutrals and l-HC7H+ is observed after deposition of C7H3 at \( \sim 90 \) eV, a higher kinetic energy. This indicates that fragmentation of C7H3+ with \( \sim 90 \) eV deposition energy is mild and only one hydrogen atom is removed. Enhancement of the absorptions of E+ in higher kinetic energy experiments suggests that besides the fragmentation, rearrangement of hydrogen atoms takes place upon the collisional impact of C7H3+ with the neon surface. Isomer E+ is a secondary product as E+ lies 450 kJ mol\(^{-1}\) above the lowest energy isomer A+, and is unlikely to be formed in the source.

Assignment of the absorption systems of the C7H3+ and C7H3+ isomers is based on CASPT2 calculations of the vertical excitation energies. The assignment is supported by comparison of the calculated harmonic vibrational frequencies with the ones derived from the spectra. The first observation and identification of the electronic absorptions of the C7H3+ and C7H3+ isomers in a neon matrix is a starting point for gas phase studies. The knowledge of electronic transitions of the C7H3+ and C7H3+ isomers provides the means for their in situ monitoring in flames and combustion processes and could lead to a better understanding of polycyclic hydrocarbon formation.

### Acknowledgements

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### References
