Electronic and infrared absorption spectra of linear and cyclic C$_6^+$ in a neon matrix

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Electronic and infrared absorption spectra of mass-selected C$_6^+$, generated by dissociative electron impact ionization of C$_6$Cl$_6$ and C$_6$Br$_6$, have been recorded in 6 K neon matrices. Linear and cyclic forms of C$_6^+$ have been observed. The $^2$II$_u$→X $^2$II$_g$ electronic transition of linear C$_6^+$ has its origin band at 646 nm whereas for the (2) $^2$B$_2$→X $^2$A$_1$ system of the cyclic isomer it lies at 570 nm. An infrared active fundamental mode in the ground electronic state of C$_6^+$ is observed at 2092 and 1972 cm$^{-1}$ for the linear and cyclic isomer, respectively. © 2004 American Institute of Physics.

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INTRODUCTION

The bare carbon cations C$_n^+$ are of interest in terrestrial and space environments as well as from a fundamental point of view. They are reactive intermediates in flames and discharges through organic vapors and they also play a role in astrochemical processes in circumstellar shells around carbon stars and interstellar clouds.1,2

Experimentally they have been mainly generated by laser ablation of graphite and studied by mass spectrometry3–6 regarding their structure, energetics, stability,7–12 and reactivity with simple molecules.13–19 These have revealed that the small linear and cyclic C$_n^+$ isomers have similar energies but their relative stability changes depending on the theoretical method used.1,2

However, the carbon cations remain exotic objects in terms of spectroscopy in contrast to their neutral and anionic counterparts.1,2 The reports are limited to the simplest (C$_2^+$)23 and large fullerene cations (C$_{60}^+$, C$_{70}^+$).20–28 The present contribution enlarges this very short list and reports the observation of the electronic and infrared transitions of mass-selected C$_6^+$ ions isolated in 6 K neon matrices.

EXPERIMENT

The experimental setup has been described previously.29 The C$_6^+$ cations were generated in a hot cathode-discharge ion source from perchloro- or perbromobenzene. C$_6^+$ was selected from a mixture of ions formed in the source by means of a quadrupole mass filter. In order to get a sufficient ion current for the matrix production, the resolution of the mass filter was lowered and the ions which differed by ±2 amu from C$_6^+$ were not separated.

Beams of C$_6^+$ with 10–30 nA current and kinetic energy of about 50 eV were codeposited with an excess of neon onto a rhodium coated sapphire substrate held at 6 K. Absorption spectra were subsequently measured in the 230–1100 nm range. The effective optical path of the light through the matrix using a waveguide technique was about 2 cm. The infrared spectra were measured by doubly reflecting light from a Fourier-transform infrared spectrometer through the matrix achieving a path length of ~1 mm.

RESULTS AND DISCUSSION

Figure 1 shows various recordings of electronic absorption spectra of mass-selected species (72±2 amu) in neon matrices. Trace (a) is from a previous study using a cesium sputter source and the absorption bands marked are due to the (1) $^2$II$_g$→X $^2$II$_u$ electronic transition of linear C$_6^+$.

Traces (b) and (d) are the present measurements. Using hexachlorobenzene as precursor and C$_6^+$ selection trace (b) is observed. Trace (c) is the $^3$Σ$^-$$^-$→X $^3$Σ$^-$$^-$ absorption system of linear C$_6$ identified in a previous study.30 C$_6$ is already present in trace (b) as a result of neutralization of the cations with electrons. The matrix remains electrically neutral during the deposition because the positive charge is compensated by anions formed in electron attachment processes with impurity molecules (e.g., H$_2$O, CO$_2$). After the first few seconds of deposition, positive charge builds up which repels further cations arriving. Those with about 50 eV kinetic energy hit metal surfaces and release free electrons. These are attracted to the matrix and lead to a partial neutralization of the cations. Some electrons are captured by neutral molecules and form anions, the reason that C$_6^-$ is also present in the matrix [trace (b)]. Such processes take place continuously during the whole matrix growth. In addition to the l-C$_6^-$ bands and the neutral l-C$_6$, system several new absorption peaks at 646, 632, 570, and 520 nm are seen. Because these absorptions are absent in traces (a) and (c), and due to the mass-selection of C$_6^+$, they are attributed to ions.
precursors were mass selected and deposited. None of the linear C$_6^+$ ions obtained previously using a cesium sputter ion source (see Ref. 30). Trace (a) is observed after deposition of C$_6^+$ generated from C$_6$Cl$_6$ in the hot cathode ion source. Trace (c) shows the $\Sigma^+_g - \Sigma^+_u$ system of linear C$_6^+$ obtained after UV irradiation of the matrix containing C$_6^+$ ions. Trace (d) is the absorption of C$_4$Cl$^+$ produced from C$_4$Cl$_6$. The bands of C$_6^-$, marked with $\psi$ in trace (a) and those of linear neutral C$_6^+$, marked with $\eta$ in trace (c) were normalized in such a way that their intensities are the same as in trace (b). $\star$ is the band of cyclic C$_6^+$.

In order to exclude the possibility that the selected ions with $72 \pm 2$ amu are not C$_6^+$ but C$_5$Cl$^+$, trace (d) was recorded. For this C$_5$Cl$_6$ was introduced into the ion source and C$_5$Cl$^+$ mass selected. No absorptions are seen at the positions of the four new peaks of trace (b).

In order to exclude the possibility that the bands seen in Fig. 1(b) originate from fragments of C$_6^+$ (C$_n^+ n=4,5$, $p=\pm 1$), C$_4^+$ and C$_5^+$ generated from C$_4$Cl$_6$ and C$_5$Cl$_6$ as precursors were mass selected and deposited. None of the bands seen in Fig. 1(b) (except C$_3$) were observed in the spectra. The results of these experiments indicate that the bands at 646, 570, and 520 nm originate from a species with six carbon atoms. The disappearance of these bands under ultraviolet (UV) irradiation ($\lambda<305$ nm) and the simultaneous growth in intensity of the C$_6$ bands [Fig. 2(b)] indicates that these three absorption peaks are due to C$_6^-$ or C$_6^-^-$ ions.

C$_6^+$ was also generated from C$_6$Br$_6$. Figure 2 compares the spectra obtained from C$_6$Cl$_6$ [traces (a) and (b)] and C$_6$Br$_6$ [traces (c) and (d)] as precursors. The bands of C$_6^-$, linear C$_6^-$ and the origin band of C$_3$ dominate. In addition, a moderately intense band at 570 nm is present, whereas the 646 and 520 nm ones are absent. No other bands were detected in the 650–$1100$ nm range, and only the absorption peaks of 1-C$_6^-$ and C$_3$ between 230 and 400 nm were observed as when using the C$_6$Cl$_6$ precursor. The peak at 570 nm vanishes and the bands of 1-C$_6^-$ diminish substantially after irradiation of the matrix with UV photons, whereas those of 1-C$_6^-$ grow in intensity [Fig. 2(d)]. From this it is concluded that the bands seen at 520, 570, and 646 nm in Fig. 1(b) originate from at least two different C$_6^-$ ($p=\pm 1$) ions.

The sign of the charge of carbon ions responsible for these three absorption bands was determined by deposition of mass-selected C$_6^+$ in a neon matrix in the presence of CCl$_4$ (CCl$_4$–Ne ratio of 1:2000), which acts as an electron scavenger. The absorption spectrum observed is shown in Fig. 3(a). In spite of 50% larger C$_6^+$ current in comparison with the experimental conditions without the electron scavenger [Fig. 2(a)], the bands of C$_6^-$ are two times weaker, the band at 520 nm is absent and the ones at 646 and 570 nm are much stronger than expected. After irradiation of the matrix with UV photons the bands of 1-C$_6^-$ and the systems with the onsets at 646 and 570 nm decrease drastically [Fig. 3(b)]. Due to the absence of the band at 520 nm in the experiment...
with CCl₄ it is concluded that this absorption is most likely due to a nonlinear isomer of C₆⁺. CCl₄ competes with other molecules present in a matrix in the capture of free electrons. As a result the bands of l-C₆⁻ become weaker in the presence of a scavenger, whereas the 520 nm absorption of the other isomer of C₆⁻ is absent due to its low electron affinity.

The band systems with the onsets at 570 and 646 nm originate from two different isomers of C₆⁺ (cyclic and a linear one). This conclusion is based on the behavior of these bands under UV irradiation and the presence of the electron scavenger [compare traces (a) and (c) in Fig. 2]. The bands at 570 and 646 nm have a similar bleaching behavior with respect to UV photons as is typical for cations. The bands of C₆⁺ are stronger in the matrix doped with CCl₄ because it captures electrons and thus reduces their recombination with C₆⁻. The 570 and 646 nm bands are present in the spectrum recorded after deposition of C₆⁺ with C₆Cl₆ as a precursor [Fig. 2(a)], but with C₆Br₆ only the 570 nm band is observed [Fig. 2(c)].

Though the intensity of the band at 570 nm in the spectrum of C₆⁺ [Fig. 2(a)] is much weaker than at 646 nm, the isomer that is responsible predominates in the matrix. The UV light-induced decay of the 570 nm absorption gives rise to the concurrent intensity increase of the bands of l-C₆⁻. The absorbance of the origin band of l-C₆⁻ increases by a factor of 3 relative to the initial absorbance of the peak at 570 nm. Linear C₆ is also produced in the matrix as a result of photodetachment of electrons from C₆⁻ anions. However, the decay of the bands of l-C₆⁻ can only account for a very small fraction of the increase in the absorbance of l-C₆⁻ because the oscillator strength for the origin band of l-C₆⁻ is an order of magnitude larger than for l-C₆⁻. 32,33

It is difficult to conclude exclusively from the spectroscopic data which isomer of C₆⁺ absorbs at which wavelength. However, an indication comes from the ion mobility and bimolecular reactivity studies on C₆⁺ ions. 11,13,14,19 These show that the predominant form of C₆⁺ is the linear isomer irrespective of how C₆⁺ is produced. Thus, the reaction of C₆⁻ with N₂O in a neon matrix was studied.

Mass-selected C₆⁺ cations generated form C₆Cl₆ or C₆Br₆ were deposited in a neon matrix containing 1% of N₂O. The resulting electronic absorption spectra are shown in Figs. 3(c) and 3(f) with C₆Cl₆ as precursor. Apart from the C₆⁺ bands at 570 and 646 nm a strong system [marked with ★ in Fig. 3(c)] with the onset at 558 nm is clearly discernible. This band system vanishes upon UV irradiation, which suggests that it originates from the C₆O⁺, or C₆N⁺, cation according to the gas-phase reaction C₆⁺ + N₂O. The bands of C₆⁺ also diminish substantially [Fig. 3(d)] whereas the ones of neutral linear C₆ and C₃ grow in intensity. The appearance of the new bands in the spectrum of C₆⁺ in the presence of N₂O [Fig. 3(c)] as well as the comparison of the intensity ratio of the 570 and 646 nm peaks shown in Fig. 3(a), leads to the conclusion that the isomer of C₆⁺ which absorbs at 646 nm reacts with N₂O in a 6 K matrix.

In contrast to the situation with C₆Cl₆ as precursor, the C₆⁻ isomer generated from C₆Br₆ does not react with N₂O in a neon matrix [Fig. 3(f)]. This is composed of the strong band system of C₆⁻ with the origin at 570 nm. The bands of neutral linear C₆ are barely seen. Thus, N₂O acts as an electron scavenger and the trapping efficiency of C₆⁺ in the matrix is close to unity (the recombination of cations with electrons is negligible in this case). No other bands were observed in this spectrum except those at 604 and 516 nm, which are due to hydrogenated C₆⁺ cations (e.g., H₆C₅⁺), and are present in the matrix as a result of contamination of the C₆Br₆ sample used for generation of C₆⁺ with C₆H₂Br₄ because the mass selection was ±2 amu. Irradiation with UV photons leads to a significant decrease of the C₆⁺ bands relative to those of the linear C₆ [Fig. 3(e)].

The reaction of C₆⁺ with N₂O reveals that the 646 nm isomer of C₆⁺ is reactive, whereas the 570 nm one is not. Gas-phase reactivity studies indicate that the linear isomer of C₆⁺ is reactive. Therefore, the band system with the onset at 646 nm originates from linear C₆⁺, whereas that at 570 nm belongs to cyclic C₆⁺. In our hot-cathode ion source, contrary to the experiments reported in the literature, 19 the c-C₆⁺ is produced in a major quantity from C₆Cl₆ as well as C₆Br₆ precursors.

Harmonic frequencies have been calculated by means of density functional theory (DFT) using the Becke three-parameter Lee-Yang-Parr (B3LYP) functional in conjunction with the correlation consistent polarized valence double zeta (cc-pVDZ) basis set for linear C₆₀ and cyclic (C₆₂) C₆⁺ in their ground electronic states. 34 By comparison with these values (given in the footnote to Table I) vibrational assignments in the excited electronic states have been made using the same numbering of modes. For the l-C₆⁺ there are three totally symmetric modes (σ) which can be excited in transitions from the lowest vibrational level of the ground electronic state where the total population is concentrated at 6 K. The electronic spectrum of l-C₆⁺ shows the single excitation of the v₁ and v₃ modes, as well as v₁ (σ) in double quanta. In case of cyclic C₆⁺ (C₆₂) there are five totally symmetric modes (a₁) and the spectrum shows the excitation of three of

<table>
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<tr>
<th>λ (nm)</th>
<th>v (cm⁻¹)</th>
<th>Δv (cm⁻¹)</th>
<th>Assignment²</th>
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<td>645.8</td>
<td>15484</td>
<td>0 0 0</td>
<td>2²Π₁ ²Π₀ l-C₆⁻</td>
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<tr>
<td>632.5</td>
<td>15811</td>
<td>327 7 0</td>
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<tr>
<td>619.5</td>
<td>16143</td>
<td>659 3 0</td>
<td>³Π₁ ²Π₁ l-C₆⁻</td>
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<td></td>
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<tr>
<td>547.1</td>
<td>18277</td>
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<td></td>
</tr>
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<td>569.6</td>
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<tr>
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<td>18188</td>
<td>630 5 0</td>
<td>(2) ³Π₂ ²Π₁ l-C₆⁻</td>
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<tr>
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<tr>
<td>508.9</td>
<td>19560</td>
<td>2092 1 0</td>
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</tr>
<tr>
<td>493.9</td>
<td>20248</td>
<td>2690 1 0</td>
<td></td>
</tr>
<tr>
<td>467.0</td>
<td>21418</td>
<td>3856 1 0</td>
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²Using numbering of the calculated frequencies (cm⁻¹) for the ground state from Ref. 34. l-C₆⁻: v₁(σ) = 2200, v₁(π) = 1584, v₁(σ) = 662, v₁(π) = 2068, v₁(σ) = 1171, v₁(π) = 689/607, v₁(π) = 205/172, v₁(π) = 397/362, v₁(π) = 99/1; l-C₆⁻: v₁(π) = 2178, v₁(π) = 1236, v₁(π) = 1195, v₁(π) = 661, v₁(π) = 563, v₁(π) = 459, v₂(π) = 476, v₂(π) = 364, v₂(π) = 2076, v₁(π) = 1307, v₁(π) = 1307.
these fundamentals. The highest frequency is presumably the $v_1(a_1)$ mode and the other two are $v_2(a_1)$ or $v_3(a_1)$ and $v_4(a_1)$ or $v_5(a_1)$. The calculations predict these pairs to have similar frequencies.

Irradiation of $c$-$C_6^+$ with UV photons leads to the appearance of $l$-$C_6$ in the matrix. Apart from the bands of $l$-$C_6$ no new absorptions grew in intensity upon UV irradiation which could be assigned to $c$-$C_6$. The electronic absorption spectrum of $c$-$C_6$ is unknown, but theory predicts an electronic transition at 2.96 eV. There are two possible reasons for the absence of the $c$-$C_6$ bands. One could be a reaction of $c$-$C_6^+$ with electrons produced by photodetachment from anions in the matrix leading to an exited state of $c$-$C_6$ followed by a ring opening. The other could be a small oscillator strength of the $c$-$C_6$ transition. The close to unity conversion yield of $c$-$C_6^+$ to $l$-$C_6$ allows an estimation of the oscillator strength of the electronic transition of $c$-$C_6^+$ with reference to that of $l$-$C_6$; the former is comparable or almost two times weaker.

In the case of $l$-$C_6^+$ we cannot separate the contribution of the cyclic form to the increase of the intensity of the band system of $l$-$C_6$ upon UV irradiation, because $l$-$C_6^+$ coexists in a large excess of $c$-$C_6$. Apart from the direct UV photodissociation, $l$-$C_6^+$ also undergoes dissociative recombination with free electrons, leading to the $C_3$ fragment. This latter reaction supports the proposed assignment because the fragmentation of $l$-$C_6$ to $C_3$ is energetically more favorable than from $c$-$C_6$ where two C–C bonds must be broken.

*Ab initio* multireference configuration interaction (MRCI) calculations predict that the lowest exited state of linear $C_6^+$ has $^3\Pi_u$ symmetry and two electronic transitions at 2.57 and 2.94 eV are expected, whereas the strongest vertical electronic transition (2) $^2B_2^\rightarrow X^2A_1$ for the $c$-$C_6^+$ is calculated at 3.08 eV. These theoretical results support the assignment of the 646 nm band to the $^{2}\Pi_u^\rightarrow X^{2}\Pi_u$ electronic transition of $l$-$C_6^+$. The calculations overestimate the excitation energy to the $^{2}\Pi_u$ electronic state by 0.65 eV; the discrepancy is larger than the likely error quoted. However, the results of extensive MRCI *ab initio* calculations agree better, predicting the energy of the allowed electronic transition at 1.88 eV close to the experimental value of 2.19 eV.

The band system originating at 570 nm is assigned to the (2) $^2B_2^\rightarrow X^2A_1$ electronic transition of $c$-$C_6^+$. The difference between calculated vertical and the experimental transition energy is much larger (0.9 eV) in this case. The reason for this large difference appears to lie with geometry change in the two electronic states and the multiconfigurational complete active space self-consistent (CASSCF) method leads to a value of 2.39 eV for this transition.

In order to corroborate the above assignment of the electronic absorption bands to a specific form of $C_6^+$, infrared spectra were also recorded. The section of the infrared (IR) spectrum around 2000 cm$^{-1}$ of mass-selected $C_6^+$ generated from $C_6Br_6$ is shown in Fig. 4(a) (solid line). The dotted line represents the IR spectrum observed after UV irradiation of the matrix. Three bands at 1972, 1962, and 1959 cm$^{-1}$ are clearly seen [Fig. 4(a)]. The band at 1972 cm$^{-1}$ decreases upon UV irradiation whereas the ones at 1959 and 1962 cm$^{-1}$ grow in intensity. The behavior of these bands closely mimics the electronic absorption of the $c$-$C_6^+$ cation (at 570 nm) and of $l$-$C_6$ (at 511 nm) upon UV radiation [Fig. 4(b)].

The band at 1959 cm$^{-1}$ was observed previously in a neon matrix and assigned to the $\nu_4$ antisymmetric mode of $l$-$C_6$. The band at 1962 cm$^{-1}$ most likely originates from the occupation of another site in the matrix. The earlier results indicate that the 570 nm electronic system and the IR band at

![Figure 4. IR bands of cyclic $C_6^+$, linear $C_6$ [solid line in (a)] and linear $C_6^+$ [solid line (c)] observed after deposition of mass-selected $C_6^+$ produced from $C_6Br_6$ and $C_6Cl_6$, respectively. Dotted lines show the same bands recorded after subsequent irradiation with UV photons ($\lambda$ < 305 nm). The photochemical behavior of the electronic absorption bands of linear $C_6$, cyclic $C_6^+$, and linear $C_6^+$ is shown in traces (b) and (d). They were measured with the same matrices as the IR bands. Solid lines show the spectra recorded after deposition of mass-selected $C_6^+$, dotted ones after UV irradiation.](image)
TABLE II. Experimental and calculated electronic transition energies and vibrational frequencies of linear and cyclic C\textsubscript{6}\textsuperscript{+}.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Electronic state</th>
<th>(T_e / \text{eV})</th>
<th>(v / \text{cm}^{-1})</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>(l\text{-C}_6\text{+})</td>
<td>(X^2\Pi_u)</td>
<td>1.92 2.57, a 1.88</td>
<td>2146</td>
<td>(\nu_1(\sigma_g))</td>
</tr>
<tr>
<td>(l\text{-C}_6\text{+})</td>
<td>(2^3\Pi_u)</td>
<td>2092 2068\textsuperscript{c}</td>
<td>2069</td>
<td>(\nu_3(\sigma_u))</td>
</tr>
<tr>
<td>(c\text{-C}_6\text{+})</td>
<td>(X^2\Sigma^+_g)</td>
<td>0</td>
<td>164</td>
<td>(\nu_3(\sigma_u))</td>
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<tr>
<td>(c\text{-C}_6\text{+})</td>
<td>(2^3\Pi_u)</td>
<td>1972 2076\textsuperscript{c}</td>
<td>630</td>
<td>(\nu_2(\sigma_g)) or (\nu_2(\sigma_g))</td>
</tr>
<tr>
<td>(c\text{-C}_6\text{+})</td>
<td>(2^3\Sigma^+_g)</td>
<td>1297</td>
<td>(\nu_2(\sigma_g)) or (\nu_2(\sigma_g))</td>
<td></td>
</tr>
<tr>
<td>(c\text{-C}_6\text{+})</td>
<td>(2^3\Pi_u)</td>
<td>2092</td>
<td>(\nu_3(\sigma_u))</td>
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</table>

\textsuperscript{a}Reference 23.
\textsuperscript{b}Reference 36.
\textsuperscript{c}Reference 22.

1972 cm\textsuperscript{-1} originate from the same molecule, namely \(c\text{-C}_6\text{+}\). Photoconversion of \(c\text{-C}_6\text{+}\) in the matrix leads to \(l\text{-C}_6\text{+}\). We did not observe the IR band at 1700 cm\textsuperscript{-1} which was assigned\textsuperscript{38} a neutral cyclic \(C_6\text{+}\). This is consistent with the failure to detect the visible spectrum, as discussed earlier.

Another part of the IR spectrum of \(C_6\text{+}\) trapped in a neon matrix containing CCl\textsubscript{4} as electron scavenger is seen in Fig. 4(c) (solid line), and after UV irradiation (dotted line). The spectra were recorded with the same matrix as for the electronic spectra of Figs. 3(a) and 3(b). Apart from the bands at 1972, 1962, and 1959 cm\textsuperscript{-1} observed with \(C_6\text{Br}_6\) as the precursor, an additional band with a doublet structure (at 2087.3 and 2092.1 cm\textsuperscript{-1}) is apparent. One component of this doublet (2087.3 cm\textsuperscript{-1}) vanishes entirely, whereas the second diminishes substantially upon irradiation with UV photons. In addition, after irradiation the 2043 cm\textsuperscript{-1} band of \(C_3\text{+}\) appears in the IR spectrum [not shown in Fig. 4(c)]. From comparison of the traces in Figs. 4(c) and 4(d) we can see that the origin band of the electronic transition of \(l\text{-C}_6\text{+}\) at 646 nm behaves exactly as the 2087.3 and 2092.1 cm\textsuperscript{-1} IR doublet. This indicates that the electronic system with the onset at 646 nm and this IR transition originate from \(l\text{-C}_6\text{+}\). Moreover, \(l\text{-C}_6\text{+}\) recombines dissociatively with an electron and forms neutral \(C_3\) in the matrix upon absorption of an UV photon.

The fundamental modes in the ground and excited electronic states of \(l\text{-C}_6\text{+}\) and \(c\text{-C}_6\text{+}\) inferred from the IR and electronic absorption spectra are given in Table II. The experimental and theoretical electronic transition energies of these cations are also collected there. The normal modes of linear and cyclic \(C_6\text{+}\) have been calculated by a discrete Fourier transform method.\textsuperscript{22} These calculations predict the antisymmetric \(\nu_1(\sigma_g)\) mode of \(l\text{-C}_6\text{+}\) and \(\nu_9(\sigma_g)\) vibrations of \(c\text{-C}_6\text{+}\) at 2068 and 2076 cm\textsuperscript{-1}, respectively. The calculated vibrational frequencies of the \(C_6\text{+}\) isomers are similar and associated with a large error.

CONCLUSIONS

Cyclic \(C_6\text{+}\) is solely formed in the hot cathode ion source with \(C_6\text{Br}_6\) as the precursor, whereas from \(C_6\text{Cl}_6\) the cyclic and linear \(C_6\text{+}\) isomers are produced. The linear isomer of \(C_6\text{+}\) has the \(2^3\Pi_u \rightarrow X^2\Pi_u\) electronic transition with origin band at 646 nm. Cyclic \(C_6\text{+}\) also absorbs in the visible with origin band at 570 nm for the \(2^3\Pi_u \rightarrow X^2\Sigma^+_g\) transition.

Irradiation of \(c\text{-C}_6\text{+}\) with UV photons leads to the appearance of \(l\text{-C}_6\text{+}\) in a matrix, whereas \(l\text{-C}_6\text{+}\) fragments of \(C_3\) as a result of dissociative recombination with electrons liberated from weakly bonded anions. Linear \(C_6\text{+}\) reacts with N\textsubscript{2}O in the neon matrix whereas the cyclic isomer is unreactive. The observation and identification of the electronic transition of \(l\text{-C}_6\text{+}\) and \(c\text{-C}_6\text{+}\) in 6 K matrices opens the way for spectroscopic studies of these astrophysically important ions in the gas phase.

ACKNOWLEDGMENT

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