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Communication: Electronic Transition of the l-C_6^+ Cation at 417 nm

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Abstract

A new electronic transition is reported for the linear C_6^+ cation with an origin at 416.8 nm. This spectrum can be compared to the matrix isolation spectra at lower energies reported previously by Fulara et al. (J. Chem. Phys. **123**, 044305 (2005)), which assigned linear and cyclic isomers, and to the gas phase spectrum reported previously by Campbell and Dunk (Rev. Sci. Instrum. **90**, 103101 (2019)), which detected the same cyclic-isomer spectrum reported by Fulara. Comparisons to electronically excited states and vibrations predicted by various forms of theory allow assignment of the spectrum to a new electronic state of linear C_6^+. The spectrum consists of a strong origin band, two vibronic progression members at higher energy and four hot bands at lower energies. The hot bands provide the first gas phase information on ground state vibrational frequencies. The vibrational and electronic structure of C_6^+ provide a severe challenge to computational chemistry.

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Small carbon atom clusters provide fascinating examples of molecular structure and bonding.[1-6] As cluster size increases, linear chains, rings and eventually three dimensional cages are produced.[7] Carbon clusters have been detected in space, and are believed to be key players in astrochemistry.[8-17] Since the detection of C_{60} and its cation in space, the connection of carbon molecules to interstellar chemistry has become all the more compelling.[18-23] Early laboratory measurements on carbon clusters employed various forms of mass spectrometry.[24-44] Rare gas matrix isolation techniques provided some of the first infrared and UV-visible spectroscopy.[2,3,5,6,45-50] Gas phase spectroscopy measurements have been successful for neutral carbon clusters,[51-58] and some anions,[59-66] but the data for carbon cluster *cations* is very limited.[67-70] Extensive computational studies have targeted carbon clusters.[2-6,38,71-77] These studies are challenging because the electronic structure of carbon clusters has issues with strong correlation, symmetry breaking, biradical character, and multireference behavior. Benchmark experiments are therefore needed for vibrational and electronic states of small carbon clusters. In this report, we present new electronic and vibrational spectroscopy for the C_6^+ cation.

Until recently, the only spectroscopy on carbon cluster cations was matrix isolation infrared and UV-visible measurements on the C_n^+ (n = 5–9) species,[45-47] and that on C_{60}^+.[48,49] Cryogenic ion trap experiments by Maier and coworkers were able to obtain electronic spectra of the C_{60}^+ cation, allowing assignment of two diffuse interstellar bands.[19-23] Kappes and coworkers used fullerene fragmentation to produce larger C_n^+ species (n = 11,12,15,16,18,21) in neon matrices to study their UV-visible spectra.[50] In recent gas-phase work, Campbell and coworkers used the same methods employed for C_{60}^+ to obtain an electronic spectrum of C_6^+, which they assigned to the cyclic structure,[67] and of C_5^+ which they assigned to the linear structure.[68] Both the groups of Bieske and coworkers[69] and that of Campbell and coworkers[70] recently reported electronic spectra for the C_{2n}^+ (n = 6–14) cations measured via the photo-

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elimination of either N_2 or He "tags." There is no gas-phase spectroscopy to our knowledge for other small carbon cluster cations. Ion mobility measurements on small C_n cations and anions found evidence for both cyclic and linear structures.[40-44] Linear structures dominated for the smaller cations, whereas monocyclic rings were preferred for n =10–20.

The C_6^+ cation has been studied in rare gas matrix isolation spectroscopy by Fulara et al.[46] and this ion has been investigated computationally by several groups.[39,46,73,74,77] Both linear and cyclic isomers are predicted to be formed, with the latest computational work finding the cyclic isomer to be more stable by about 8 kcal/mol.[39] The matrix isolation spectra of Fulara et al. found bands assigned to both isomers,[46] with electronic origins at 645.8 and 569.6 nm for the linear and cyclic species, with a single IR band each at 2092 and 1972 cm^{-1}, respectively.[46] Using a cryogenic ion trap instrument, Campbell and Dunk obtained a helium-tagged spectrum with the same resonance at 570 nm assigned by Fulara to the cyclic species, with only a very weak hint of signal at the resonance near 646 nm assigned to the linear species.[67] However, gas phase ion mobility measurements by Bowers and coworkers found only the linear structure.[40,41] Apparently, the laser plasma growth of this and other small carbon clusters has a significant entropic effect favoring linear structures, whereas the ion trap conditions may favor the more stable isomer. In the only other gas phase spectroscopy to our knowledge, two-color laser photodissociation measurements were conducted several years in our lab by Ticknor.[77] Extremely weak signals were detected for two broad bands at 648 and 633 nm, at roughly the same positions as the bands in the matrix spectrum assigned by Fulara to the linear structure, but no further analysis of those spectra was possible. It is understandable that the photodissociation in this wavelength region is inefficient, because the photon energy is well below the reported 5.2 eV dissociation threshold of C_6^+ measured with collision-induced dissociation.[31,34] Neither Fulara et al.[46] nor Campbell and Dunk[67] detected any transitions at higher energies.

We report here a new gas phase electronic transition for the C_6^+ cation with an origin at 416.8 nm. The cation produced by laser ablation[79] and cooling in a supersonic expansion was mass selected in a reflectron time-of-flight spectrometer[80] and studied with photodissociation using a UV-visible OPO laser system (Continuum Horizon II; linewidth ~5 cm^{-1}). Wavelengths were calibrated with an Avantes Starline spectrometer. Photodissociation of C_6^+ in the blue visible wavelength region produced only the C_3^+ fragment, whose yield was recorded as a function of the wavelength to obtain the spectrum. This fragmentation channel has been seen in previous fixed-frequency photodissociation studies at visible and UV wavelengths.[27-29,32,33,35,44] The 5.2 eV dissociation energy[31,34] of C_6^+ is greater than the photon energy in this region. The observed photodissociation can therefore be assigned to a resonant absorption of blue light followed by absorption of one or more additional photons that leads to dissociation. This kind of resonance-enhanced photodissociation (REPD) process has been employed for many previous studies of ion spectroscopy.

Figure 1 shows the photodissociation spectrum measured in the 500–357 nm region (20,000–28,000 cm^{-1}). Scans at lower energies failed to detect any significant signal. Specifically, scans were conducted in the 570 nm region where Campbell and Dunk detected the cyclic isomer seen previously in the matrix isolation work, and near 650/630 nm where Ticknor found a weak spectrum matching that of the linear isomer also detected in the matrix isolation work. No significant signals were detected in either region. Additional unsuccessful scans were conducted in the 650/630 nm region using the OPO in combination with a Nd:YAG laser at 355 or 266 nm. The only spectra detected in these experiments is that shown in Figure 1. An intense single band is observed at 23,994 ± 5 cm^{-1} (416.8 nm), accompanied by a weak satellite 79 cm^{-1} to higher energy. Two additional weak bands are detected at energies higher than the strongest feature (25,244 and 25,647 cm^{-1}), and four slightly more intense bands are detected at lower frequencies (21,290, 21,952, 22,322 and 22,606 cm^{-1}). The positions of these bands are labeled in Figure 1. A reproducible continuous signal underlies the lower frequencies features in the range of 20,500–23,000 cm^{-1}. The much greater intensity of the 416.8 nm band suggests that it is the origin of an electronic transition. Its linewidth is about 25 cm^{-1} FWHM, which is much wider than the laser linewidth. The additional width may come from the rotational contour and/or predissociation. The higher energy bands are likely vibronic bands corresponding to excited state vibrational intervals above this origin. Their weaker intensities are caused at least in part by the lower laser power available in this region (the fundamental output switches to frequency mixing at wavelengths shorter than 400 nm). Their increased linewidths are caused by the broader laser linewidth after frequency mixing. The lower energy bands may represent hot bands arising from unquenched vibrational population in the ground electronic state. Their linewidths are 15–18 cm^{-1}. It is conceivable that these lower frequency bands represent a different excited state, but the pattern of bands fits best with the assignment of hot bands (see below). Unfortunately, experiments designed to cool these ions better to eliminate these hot bands were unsuccessful; colder conditions (e.g., with a few percent of argon added to the helium expansion gas) produced mostly larger carbon clusters and not enough C_6^+ to study. The intense origin band and weaker vibronic structure suggests that the structure of the excited state is similar to that of the ground state.

To assign this spectrum, we considered previous computational studies and performed new calculations. Although early computational studies found the linear species to be more stable,[73,74] more recent work finds that the cyclic isomer is more stable by about 8 kcal/mol.[39,77] We employed density functional theory (DFT) with the B3LYP functional and the def2-TZVP basis set, using the Gaussian 16 program package,[81] to investigate the structures and spectra of these ions. The results of these computations are presented in the Supplemental Information file.

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Our linear $D_{\infty h}$ structure has a $^2\Pi_u$ ground state with alternating bond distances indicating "acetylenic" character and our cyclic structure has a C_{2v} structure in a $^2A_1$ ground state, both consistent with previous work.[39,73,74,77] Structural parameters are consistent with those derived from earlier DFT and MRD-CI computations,[73,74] but slightly different from those derived from optimizations at the CASSCF level.[77] Consistent with earlier results,[73,74] but in contrast to later work,[39,77] our DFT computations predict the linear structure to be 9.1 kcal/mol more stable than the cyclic.

Electronic spectra for C_6^+ were investigated computationally by Haubrich et al. using MRD-CI[73] and by Gillery et al. using CASSCF.[77] These two approaches employ methods designed to deal with the multireference behavior of this system. For comparison to these results, and to evaluate its performance for future studies of larger systems, we employed time-dependent density functional theory (TD-DFT). DFT often performs surprisingly well for multireference systems, even though it is not specifically designed for this.[82,83] Table 1 and Figure 2 summarize our computational predictions for the C_6^+ spectrum compared to those from the previous work. Figure 2 shows the measured spectrum compared to the electronic transitions predicted for linear versus cyclic structures using different theoretical methods. Also included are dashed vertical lines to indicate the positions of bands seen in the matrix isolation spectrum by Fulara et al.[46] for the linear and cyclic C_6^+ structures (the cyclic spectrum was also seen by Campbell and Dunk[67]) and a section of the previous REPD spectrum by Ticknor.[78]

As shown in the figure, no single computational approach provides an accurate description of the experimental electronic spectrum. Haubrich predicted two intense $^2\Pi_u \rightarrow {}^2\Pi_g$ transitions and one $^2\Pi_u \rightarrow {}^2\Sigma_g^-$ transition for linear C_6^+ near the new spectrum, at energies of 2.57, 2.94 and 3.25 eV (20,728, 23,713, and 26,213 cm^{-1}), respectively. The band predicted at 2.94 eV is almost exactly at the position of the measured transition at 2.97 eV (23,994 cm^{-1}).

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However, nothing was predicted near the matrix spectra detected by Fulara for either the linear (1.91 eV) or cyclic structures (2.18 eV). Gillery predicted $^2\Pi_u \rightarrow {}^2\Pi_g$ transitions for linear C_6^+ at 2.58 and 2.70 eV and a $^2\Pi_u \rightarrow {}^2\Sigma_g^-$ transition at 3.25 eV (20,809, 21,777, and 26,213 cm^{-1}), all in the vicinity of the measured transition at 2.97 eV. Transitions were also predicted at 1.72 and 2.11 eV (13,783 and 17,018 cm^{-1}) near the Fulara spectrum for linear C_6^+, but nothing was predicted near the Fulara spectrum for the cyclic species. Our DFT computations predict only one strong $^2\Pi_u \rightarrow {}^2\Pi_g$ transition at 2.65 eV matching approximately the position of the new spectrum, and another (1.86 eV) near the position of the Fulara spectrum for linear C_6^+. Transitions were also predicted near the position of the Fulara spectrum for the cyclic isomer. Overall, all three computational methods predict strong transitions near the present spectrum for linear species, and all methods predict strong transitions for the cyclic species to lie at both higher energies. On this basis, it seems most likely that our spectrum corresponds to the linear structure. Surprisingly, only our DFT method finds transitions at both the position of the "red" spectrum (detected by Fulara et al. and by Ticknor) and the position of the new "blue" spectrum. The Fulara spectrum was assigned convincingly to the linear species and Ticknor found the same spectrum under conditions identical to those used here. This suggests that the new "blue" spectrum is also from the linear species. The assignment for this spectrum therefore would be to one of the $X^2\Pi_u \rightarrow {}^2\Pi_g$ transitions predicted by theory. The broad region of signal in the 20,500–23,000 cm^{-1} could conceivably be from another of the transitions predicted by Haubrich et al. or Gillery et al. in this same energy region; excitation to the repulsive wall of such an excited state could produce the broad structure.

The vibrational structure can also provide insight into the carrier of the spectrum. The higher energy bands are likely vibronic progression members, and the lower frequency bands are

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likely vibrational hot bands. To explore this further, we plotted the spectrum of the lower frequency bands in decreasing energy relative to the origin so that the intervals correspond to ground state vibrations, and compared it to the frequencies predicted by theory for linear and cyclic isomers (see Figure 3). A complete list of vibrational modes and frequencies is given in the Supplemental Information (Tables S6 and S7). Symmetric vibrations that do not change the vibronic symmetry are usually active in an allowed electronic transition, and therefore the σ_g modes for a linear structure or the a_1 modes for the cyclic structure are most likely to be active in either progressions or as hot bands. The bands corresponding to these vibrations are colored in the figure.

Figure 3 shows that a number of low frequency (<700 cm^{-1}) vibrations are predicted for both isomers, but no bands are detected with these intervals in the experimental spectrum. The bands detected all correspond to higher frequencies. This is understandable because collisional energy transfer in a supersonic beam is much more efficient for lower frequencies, and non-equilibrium populations of unrelaxed higher frequency vibrations are often found.[84] The highest fundamental predicted for the linear structure is 2186 cm^{-1} whereas that for the cyclic structure is 1806 cm^{-1}. The cyclic structure has a group of six vibrations predicted above 1100 cm^{-1}, whereas the linear structure has only four. All of the computed frequencies are unscaled harmonic values, and the problems with theory for these systems have been noted already. There are some variations in the frequencies determined here compared to those predicted by Giuffreda et al.[73] Not surprisingly, there are no examples of perfect agreement between our theory and the frequencies in the experiment. However, the distribution of bands and their frequencies match better for the linear structure, consistent with the conclusion from the electronic spectrum. The ν_8 IR-active vibration for the linear structure predicted at 2060 cm^{-1} compares to the 2092 cm^{-1} band assigned to the linear structure in the matrix IR spectrum by Fulara et al.[46] The ν_1 vibration predicted at 1806 cm^{-1} compares to that at 1972 cm^{-1} measured in the same experiment for the cyclic structure.[46]

With this information, it is possible to assign the lower energy bands to hot bands for the linear species. The 1388 cm^{-1} interval likely corresponds to the ν_9 vibration predicted at 1167 cm^{-1}. The 1672 cm^{-1} interval likely corresponds to the ν_2 vibration predicted at 1577 cm^{-1}. The 2042 cm^{-1} interval likely corresponds to either the ν_8 or ν_1 vibrations predicted at 2060 and 2186 cm^{-1}; the totally symmetric ν_1 carbon stretch is more likely to be active in an allowed electronic transition. The band at 2704 cm^{-1} is higher than any fundamental for either structure, and therefore must correspond to an overtone or combination. A reasonable assignment would be the combination of the ν_1 band at 2186 cm^{-1} with one of the 486 (ν_5), 578 (ν_4) or 660 (ν_3) cm^{-1} vibrations. The combined frequencies of these are in the right range if anharmonicity is considered. The 660 cm^{-1} vibration is a σ_g symmetric carbon framework breathing mode and its combination with the σ_g ν_1 vibration would give an overall symmetry of σ_g and would likely provide a significant Franck-Condon factor, whereas the lower frequency ν_4 or ν_5 modes correspond to bending motions. The two higher energy vibronic bands have intervals of 1250 and 1653 cm^{-1} above the 416.8 nm origin band, which seem reasonable for excited state frequencies for the ν_9 and ν_2 vibrations. An alternate assignment for the bands at frequencies below the origin is that they represent another electronic state. In this scenario, the 21,290 cm^{-1} band could be the origin, and the 21,952 and 22,606 cm^{-1} bands would be two members in a progression of the ν_3 mode at 660 cm^{-1}. However, the 22,322 cm^{-1} band would have an interval 1032 cm^{-1} above the origin, where no vibration for ground state C_6^+ is predicted, so this assignment is unlikely. Overall, the vibrational structure is best assigned to hot bands for the

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linear structure at low energy and vibronic members at higher energy, but it is clear that more reliable vibrational calculations are needed.

Another feature of the spectrum to consider is the weak band spaced 79 cm^{-1} just above the origin. It is conceivable that this interval could correspond to the spin-orbit splitting expected for a $^2\Pi_g$ excited state. If the ground state and upper state are both $^2\Pi$ states, there should be transitions between the spin-orbit levels in both states. If the ground state is cold, only the lower $^2\Pi_{1/2}$ level would be populated, and there would be two main transitions to the $^2\Pi_{1/2,3/2}$ levels of the excited state. This would produce a doublet structure, with a spacing equal to the excited state spin-orbit splitting, which may be what we observe. The 24,073 cm^{-1} band is likely detected lower in intensity than it should be because the laser power is dropping steeply in this region. If the ions are not cold, there could be overlapping transitions involving all four spin-orbit levels, which may still produce a doublet like that seen because the resolution is low. The problem is that similar doublets should also be seen for the hot band features and progressions members throughout the 417 nm system, and we do not detect these, effectively ruling out this assignment. A more likely assignment for the 24,073 cm^{-1} feature is a sequence band, which could occur higher than the origin if the excited state frequency involved is higher than the ground state frequency. The singlet bands detected throughout this system could still be caused by an excited $^2\Pi$ state, but one whose spin-orbit spacing is small relative to the laser linewidth. At the low resolution of the experiment, no additional structure beyond the broad band contour is available for a more detailed assignment.

There are clearly unresolved issues about this spectrum that raise questions about its assignment. Because the dissociation energy of this ion is 5.2 eV, the signal detected is necessarily from a two-photon (1 + 1 in the 417 nm region) absorption process. Because of this, unanticipated resonances at the second photon level may enhance the intensities of some bands

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or attenuate the intensities of others. It is conceivable that other bands are completely missing because of unfavorable resonances. If bands are missing, this would affect how the spectrum is assigned. Such effects may also influence the variable linewidths in the spectrum. To attempt to address this, several experiments varying laser conditions were conducted. The laser pulse energy (typically 3–4 mJ/pulse; unfocussed) was varied, producing no new signals nor significant changes in relative band intensities. Two-color experiments were conducted using the blue OPO together with 355 or 266 nm Nd:YAG wavelengths, but no additional bands were detected. Ions tagged with a rare gas atom such as argon would be less susceptible to intensity artifacts, but we were unsuccessful in producing tagged ions. Colder conditions, e.g., in an argon expansion, produced larger carbon clusters and eliminated the small clusters like C_6^+ from the distribution. Although it is conceivable that intensities are somehow biased, such effects should not produce bands where there are no resonances, and therefore the bands actually detected here should represent legitimate resonances for this ion. Another source of concern is why the present spectrum was not detected in the previous matrix isolation experiments of Fulara et al. It is conceivable that excited state dynamics in the matrix broadened or weakened the spectrum relative to those in other regions, and it is also conceivable that our sensitivity is better than that in the matrix. Another possibility is that this spectrum is from a metastable excited state of this ion which was not present in the matrix. Several low-lying quartet states have been predicted by theory, and if such a state were produced it could conceivably survive on the 100 μsec timescale of the molecular beam experiment, but not likely in the matrix experiment. The ion production scheme and timescales are different in the two experiments, and although we consider this unlikely, we cannot rule it out completely. Experiments using different vaporization laser wavelengths that could change the plasma chemistry produced the same spectrum. Considering these issues, it is desirable for other labs, perhaps those with ion traps where tagging is more feasible, to investigate this spectrum.

Given these caveats, the best interpretation of the present spectrum is that it corresponds to one of the predicted $X^2\Pi_u \rightarrow {}^2\Pi_g$ transitions of the linear C_6^+ cation, with vibronic bands at higher frequencies and vibrational hot bands at lower frequencies. The observation of this higher energy state not detected by Fulara et al. actually provides some clarification about the theory, since the only state detected in that work was far below the energies of the strong transitions predicted. Previous theory and the present DFT methods are all insufficient for a quantitative description of the electronic transitions or the vibrational frequencies. This is understandable because of the severe multireference character that is well known for such carbon clusters. However, the present DFT and TD-DFT methods seem to exhibit performance comparable to MRD-CI or CASSCF methods. This system, and others presently under study in our lab, should provide benchmarks for new multireference computational work.

The observation of the linear C_6^+ structure for ions produced with laser vaporization and cooled in a supersonic jet contrasts with the results of Campbell and Dunk,[67] which used cryogenic cooling and found the cyclic structure for this ion. Assuming that the latest theory is correct, the cyclic species is more stable than the linear by about 8 kcal/mol.[39,77] Apparently, the cryogenic cooling favors the production of the more stable cyclic structure, whereas the warmer growth conditions and less efficient cooling of the jet prefers the entropically-favored linear species seen also in ion mobility. An additional aspect of the less efficient cooling in the jet is that the vibrational hot bands could be observed, providing the first gas phase information about ground state vibrations.

As a last note, the astrophysical importance of carbon clusters has been well documented. In particular, these clusters have been discussed in the context of the diffuse interstellar bands

(DIBs).[6,8,13-17,85-88] The strong origin of the C_6^+ spectrum, with much weaker vibronic structure, is consistent with the kind of single band seen for many of the DIBs. Indeed, the red transition seen in matrix isolation spectroscopy by Fulara et al. was noted to be close to a known DIB feature.[46] Actually, a weak DIB has been reported at 417.6 nm, which is quite close to the present origin band at 416.8 nm.[88] The width of this DIB is 2.3 nm, which is comparable to our linewidth. Unfortunately, it appears that our wavelength position just misses that of the 417.6 nm DIB. However, if the band shape varies with temperature, it is conceivable that our "cold" spectrum could match that of the known DIB, which likely corresponds to warmer molecules.

Supplemental Information

See Supplemental Information for optimized geometries and harmonic frequencies of all computed isomers.

Data Availability Statement

The data that supports the findings of this study are available within the article [and its Supplemental Information].

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Table 1. Predicted vertical excitation energies and intensities of transitions of linear C_6^+ originating in the $^2\Pi_u$ ground state.

Level of Theory	Excited State	Vertical Excitation Energy, eV (cm^{-1})	Intensity	Source
MRD-CI	$^2\Sigma_g^+$	1.45 (11,695)	0.001†	Haubrich et al.[74]
	$^2\Sigma_g^-$	1.46 (11,776)	0.003†	
	$^2\Pi_g$	2.31 (18,631)	0.0001†	
	$^2\Pi_g$	2.57 (20,728)	0.01†	
	$^2\Pi_g$	2.68 (23,195)	0.0003†	
	$^2\Pi_g$	2.94 (23,713)	0.008†	
	$^2\Sigma_u^-$	3.25 (26,213)	0.003†	
CASSCF	$^2\Sigma_g^-$	1.72 (13,873)	0.4779*	Gillery et al.[77]
	$^2\Pi_g$	2.11 (17,018)	0.6147*	
	$^2\Pi_g$	2.58 (20,809)	0.8326*	
	$^2\Pi_g$	2.70 (21,777)	1.2918*	
	$^2\Sigma_g^-$	3.25 (26,213)	0.3533*	
B3LYP/def2-TZVp	$^2\Pi_g$	1.41 (11,372)	0.0001†	This work.
	$^2\Delta_g$	1.60 (12,905)	0.0023†	
	$^2\Sigma_g^+$	1.86 (15,002)	0.0042†	
	$^2\Pi_g$	2.65 (21,374)	0.0092†	
	$^2\Sigma_g^-$	3.83 (30,891)	0.0034†	
Experiment	$^2\Pi_g$	1.91 (15,430)		Fulara et al.;[46] Ticknor et al.[78]
	$^2\Pi_g$	2.97 (23,994)		This work.

†oscillator strength
*transition dipole moment in Debye

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Figure Captions

Figure 1. Resonance-enhanced photodissociation spectrum of the C_6^+ cation measured in the C_3^+ fragment ion mass channel.

Figure 2. Comparison of the electronic transition observed here for C_6^+ near 417 nm, and the one detected previously at 648 nm, to the predictions of different kinds of theory for the linear and cyclic isomers.

Figure 3. The comparison of the vibronic bands assigned as hot-bands to the vibrational frequencies predicted by DFT for linear versus cyclic structures. The σ_g vibrations for the linear structure and the a_1 vibrations for the cyclic structure are most likely to be Franck-Condon active in an electronic transition; these bands are colored in the figure.

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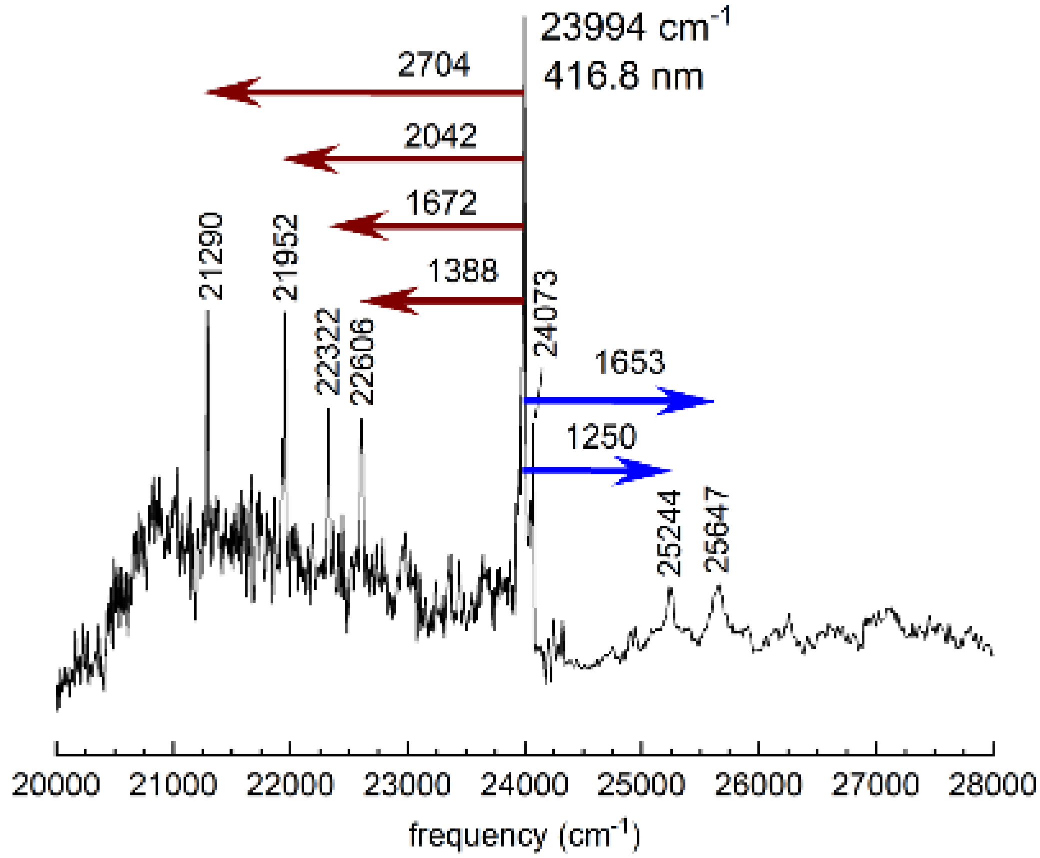

Figure 1.

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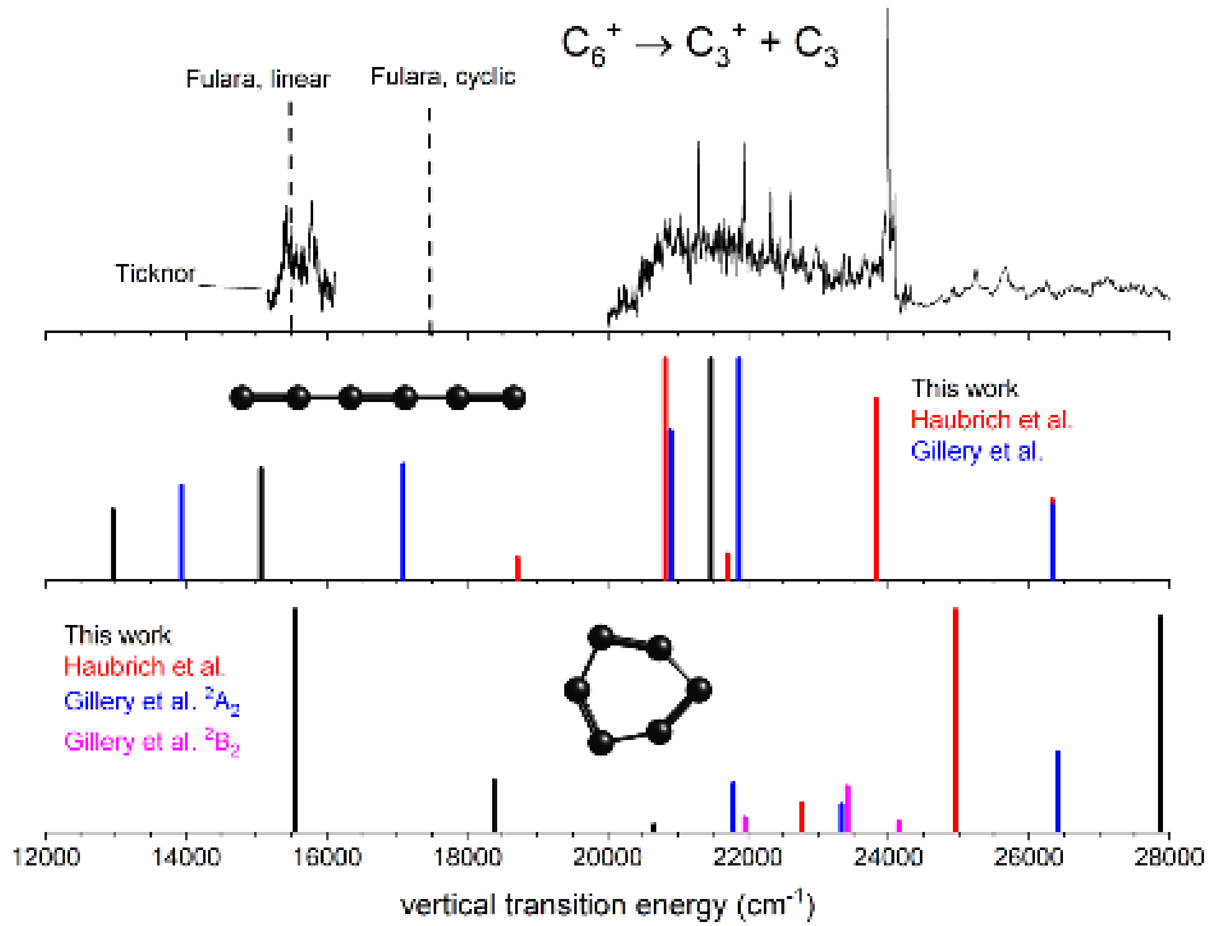


Figure 2.

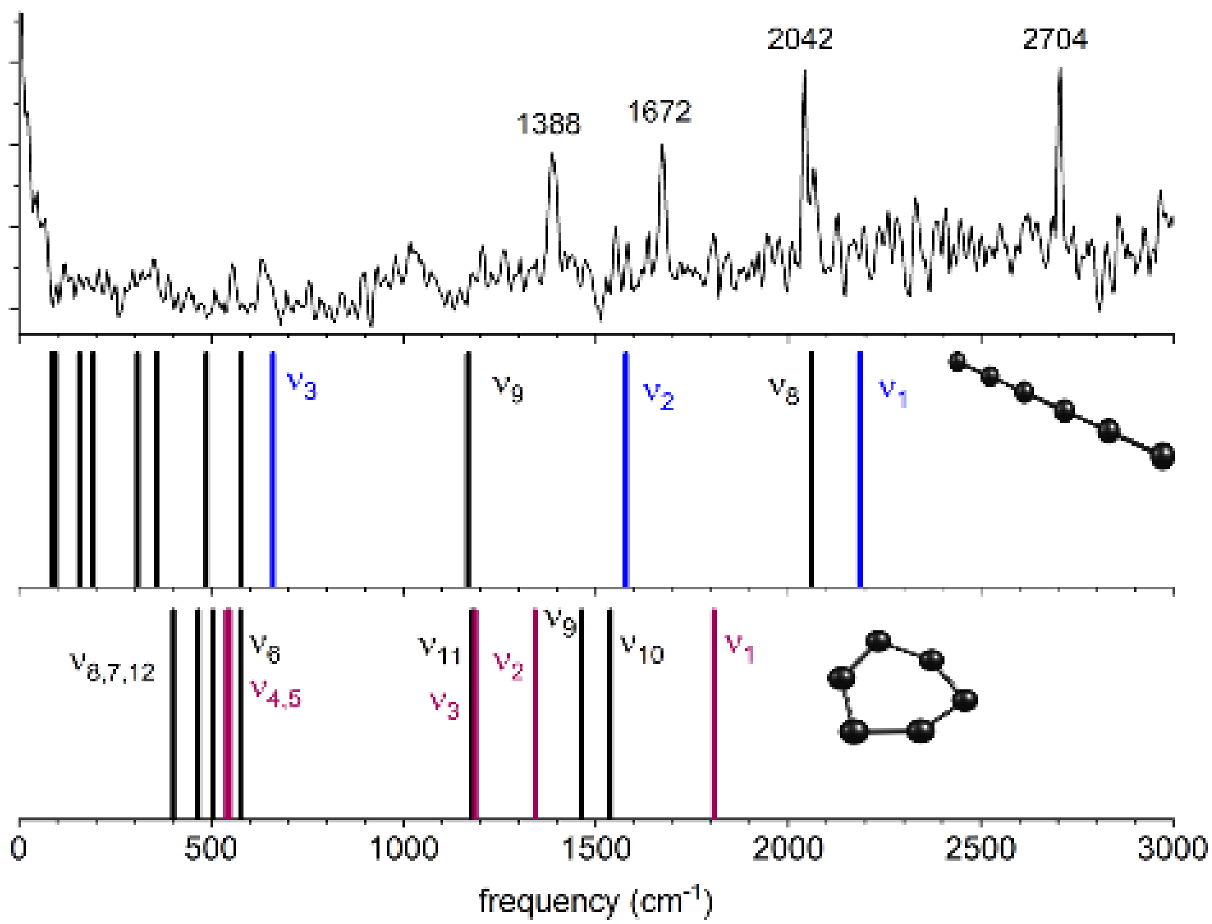
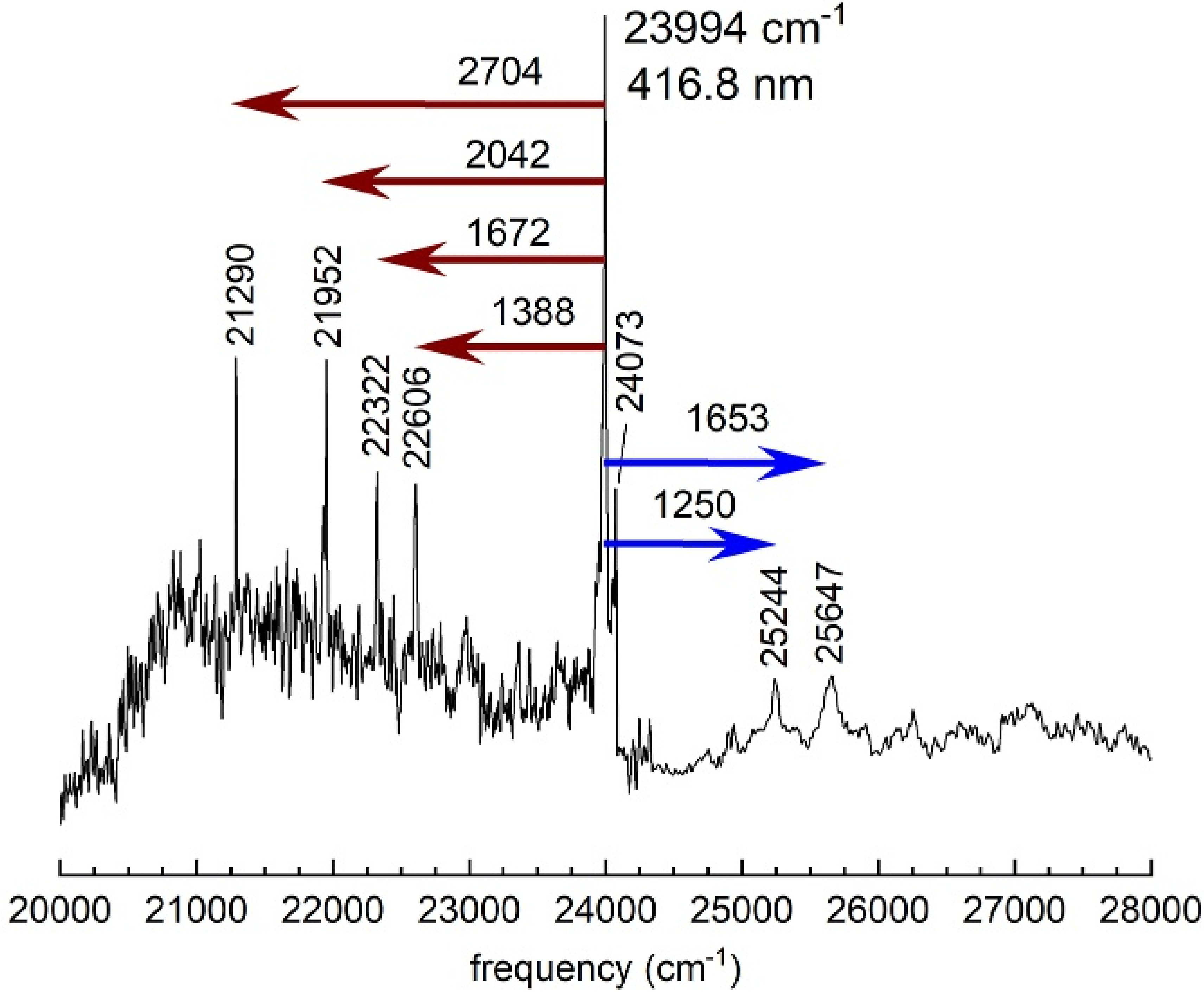

2042
2704
1388
1672
ν3
ν9
ν2
ν8
ν1
ν8,7,12
ν6
ν4,5
ν11
ν3
ν2
ν9
ν10
ν1
0
500
1000
1500
2000
2500
3000
frequency (cm-1)

Figure 3.



23994 cm-1
416.8 nm
2704
2042
1672
1388
21290
21952
22322
22606
24073
1653
1250
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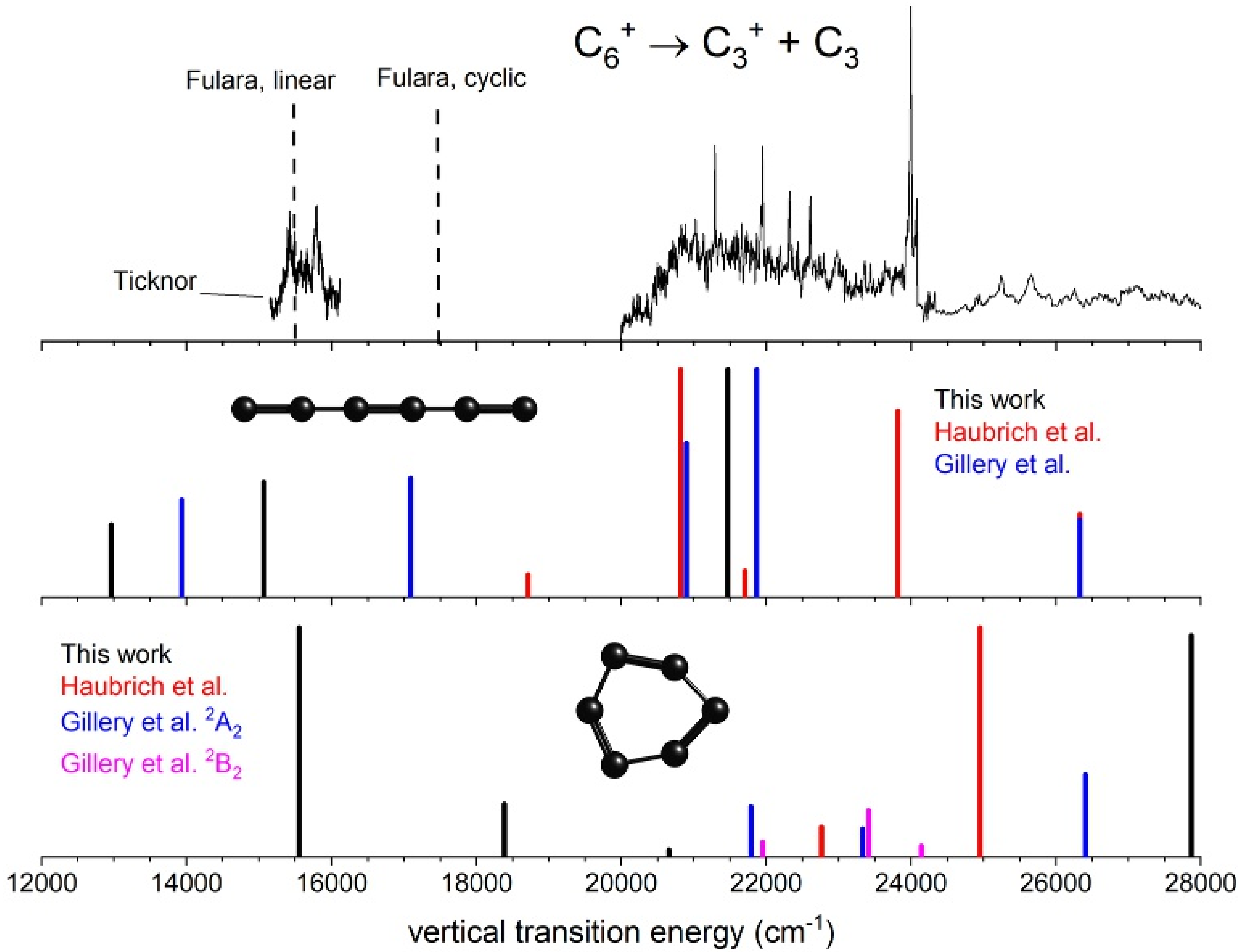
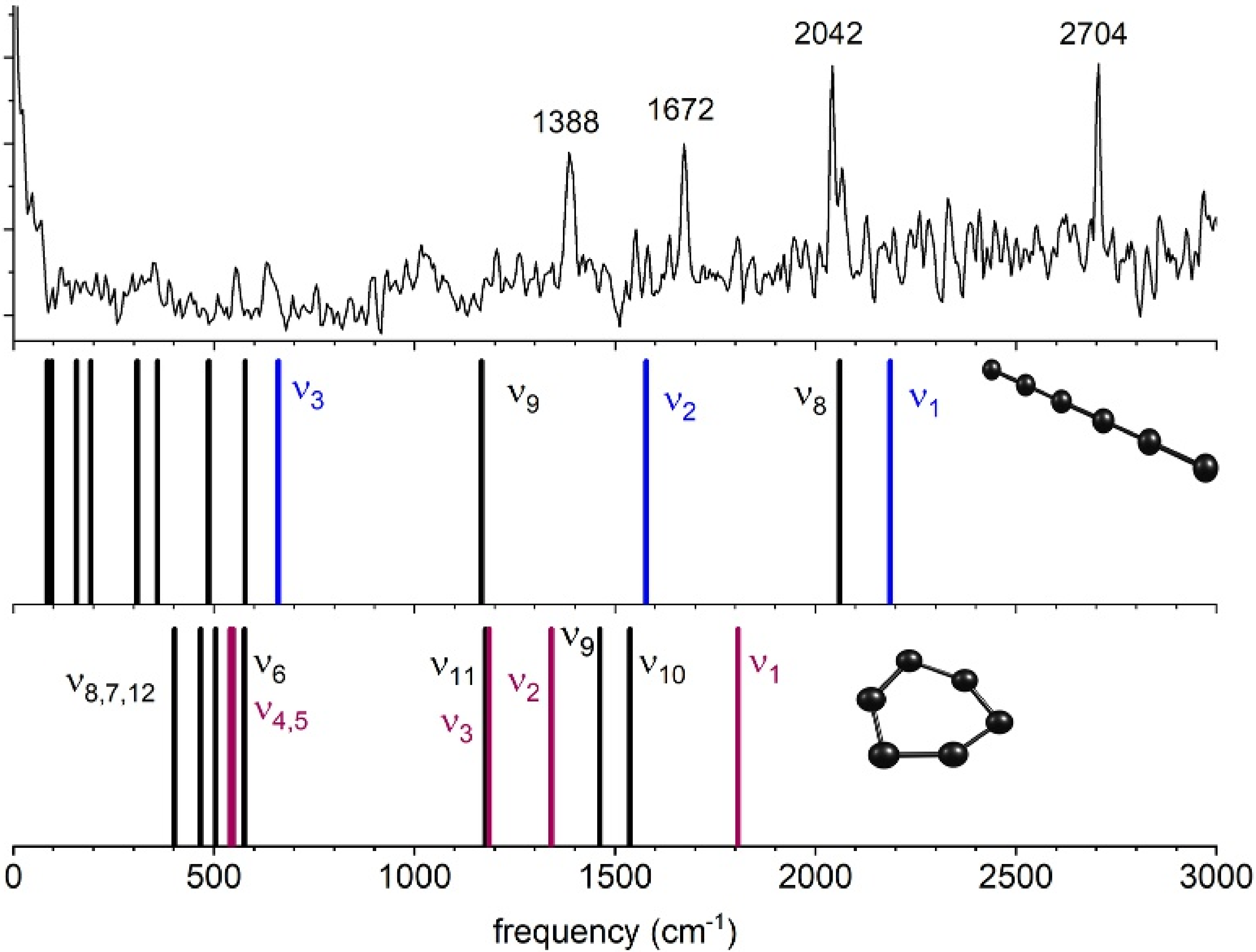
25647
20000
21000
22000
23000
24000
25000
26000
27000
28000
frequency (cm-1)



$C_6^+ \rightarrow C_3^+ + C_3$
Fulara, linear
Fulara, cyclic
Ticknor
This work
Haubrich et al.
Gillery et al.
This work
Haubrich et al.
Gillery et al. $^2A_2$
Gillery et al. $^2B_2$
12000
14000
16000
18000
20000
22000
24000
26000
28000
vertical transition energy (cm^{-1})



1388
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ν3
ν9
ν2
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ν8,7,12
ν6
ν4,5
ν11
ν3
ν2
ν9
ν10
ν1
0
500
1000
1500
2000
2500
3000
frequency (cm-1)