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# Photofragment Imaging of Carbon Cluster Cations: Explosive Ring Rupture

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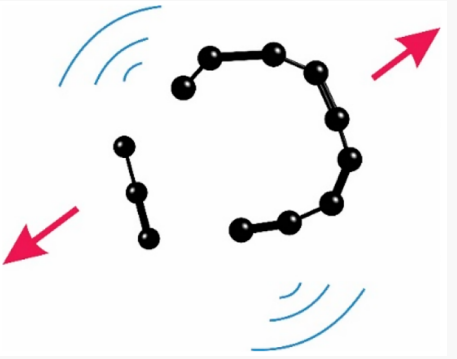
**ABSTRACT:** Carbon cluster cations ($C_n^+$) produced by laser vaporization are mass selected and photodissociated at 355 nm. Multiphoton dissociation of smaller ions leads to the elimination of neutral $C_3$, as in previous work, whereas larger clusters exhibit more varied fragmentation channels. Photofragment velocity-map imaging detects significant kinetic energy release (KER) in the various $n - 3$ cation fragments. Small cations ($n$ = 6 or 7) with linear structures produce moderate KER, whereas larger cations ($n$ = 10, 11, 12, 15, or 20) having monocyclic ring structures produce much higher KER values. Such high KER values are unanticipated, as optical excitation should produce a wide distribution of internal energies. These carbon clusters have a surprising ability to absorb multiple photons of ultraviolet radiation, achieving a state of extreme excitation prior to dissociation. The remarkable nonstatistical distribution of energy is apparently influenced by the significant ring strain that can be released upon photodissociation.





Atomic clusters of carbon have been known and studied since the early observations of $C_2$ and $C_3$ in flames and comets.[1] Larger clusters produced with more energetic ablation methods were studied in matrix isolation experiments and later in a variety of mass spectrometry and optical spectroscopy experiments.[2−27] Neutral clusters were studied initially, but later work included anions and cations. All of these species are particularly interesting for astrochemistry, including the possible connection to the unassigned diffuse interstellar bands (DIBs).[28−41] The eventual production of carbon-based materials such as fullerenes, nanotubes, and graphene continues to stimulate interest in the electronic structure and bonding energetics in pure-carbon systems.[42] In the work presented here, we investigate the photodissociation behavior of small carbon cluster cations employing photofragment imaging of mass-selected ions.

On the basis of extensive theory and experiments, small carbon clusters are known to exist as both linear-chain and cyclic isomers.[2−6,21−23,25,27,43−61] The details vary, but this is true for neutral clusters as well as cations and anions. The structures of cations have been investigated with ion mobility measurements conducted in different laboratories,[21−23,25,27] with matrix isolation spectroscopy on certain cluster sizes,[43−45] and with gas phase electronic spectroscopy.[48−50] The ion mobility of $C_n^+$ cations in several laboratories finds that the $n$ = 6 cation is linear, that $n$ = 7−9 ions are mostly linear with a small percent of cyclic structures, that the $n$ = 10 ion is mostly cyclic with a minor percent of a linear structure, and that $n$ = 11−20 ions have only monocyclic ring structures.[21−23,27] Theory finds that the ions in the $n$ = 6−9 size range are more stable in their cyclic structures, in contrast with the results of ion mobility.[26,53−56] This difference is presumably caused by the free energy at increased temperatures in the laser vaporization plasma environment where clusters grow; entropy favors linear chains over rings. Theory agrees that the $n$ = 10−20 species are more stable in monocyclic ring structures.[26,56] Recent electronic spectroscopy of tagged cations in the $C_{2n}^+$ ($n$ = 6−14) size range has been interpreted as arising from monocyclic ring structures.[49,50]

The dissociation dynamics and energetics of carbon cluster ions have been investigated extensively. Collision-induced dissociation (CID) and photodissociation experiments identified the elimination of $C_3$ as a prominent dissociation product, although other fragments ($C_2$ or $C_5$ elimination) were found for larger clusters.[10−20,27] CID indicated substantial C−C bond energies in the range of 4−6 eV,[14,17] and this thermochemistry has been supported by several computational studies.[26,52−56] However, it is recognized that thermochemistry experiments are extremely difficult on such strongly bound systems. Likewise, computational studies of bonding energetics are also challenging because of the strong multireference character of the electronic structure of these systems. For these reasons, there is still considerable uncertainty in the bond energies for carbon cluster ions. Surprisingly, early experiments found that

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photodissociation in the near-ultraviolet region was quite facile, suggesting that dissociation thresholds could be $\lesssim$3.5 eV.[10−12,15,16,18,27] However, it was later determined that these experiments involved multiphoton absorption with unanticipated high efficiency, eliminating the apparent discrepancy between different experiments. More recent work has employed ion mobility measurements prior to photodissociation to obtain structure-specific (chain vs ring) dissociation patterns for the small carbon cations.[27] Linear structures for $C_{7-10}^+$ were found to eliminate $C_3$, whereas cyclic structures eliminated both $C_3$ and $C_2$. In the work presented here, we employ photofragment imaging of mass-selected carbon cluster cations as a different approach to investigate their energetics and dynamics. This allows us to explore their efficient multiphoton absorption and possible differences in the dissociation behavior of linear-chain versus cyclic structures.

Recent work in our lab has employed the photodissociation of mass-selected ions with photofragment imaging to investigate their energetics and dynamics.[62−64] In the case of diatomic species like $Ar_2^+$, kinetic energy release (KER) in the atomic cation fragment provided a direct measure of the bond dissociation energy.[63] In metal ion−molecule complexes, selective excitation of charge-transfer excited states produced molecular ligand fragment ions with significant KER. Evidence for internal (vibrational/rotational) excitation was detected, and the resulting measurements of KER provided only upper limits to the bond dissociation energies.[62,64] In these previous cation systems, single-photon excitation was employed to define the exact amount of energy deposition. In the carbon cations, single-photon dissociation is not possible with available lasers in the near-ultraviolet range, and therefore, multiphoton excitation is required for these experiments. However, this introduces considerable uncertainty into the amount of energy deposited in these systems. Laser pulse energies great enough to cause two-photon absorption may also cause higher-order absorption, and power dependence studies in such systems are not reliable. Nevertheless, carbon clusters provide an opportunity to probe dissociation dynamics in strongly bonded cluster ion systems with known structures.

Carbon cluster cations were produced by laser ablation of a solid rod sample in a pulsed supersonic expansion of helium.[65] The effects of other expansion gases (Ar and $N_2$) were also investigated. This experiment uses the same laser vaporization method and conditions employed in previous ion mobility measurements[21−23,27] and electronic spectroscopy experiments.[48−50] Cluster structures are therefore assumed to be the same as in those experiments, i.e., linear for $n$ < 10 and monocyclic rings for $n$ = 10−20. Ions are analyzed and mass selected in a reflectron time-of-flight mass spectrometer. The mass spectra from Nd:YAG laser photodissociation at 355 nm are detected in the second flight tube of the reflectron using methods described previously.[66,67] Photofragment imaging is conducted in an instrument described previously;[62−64] it is shown in Figure S1. For this experiment, the selected ions pass through the grounded reflectron grid assembly into a second field region, where they are decelerated and excited with a Nd:YAG laser at 355 or 266 nm. Parent ions and photofragments are re-accelerated with velocity-map imaging (VMI) electrodes[68] and travel down a 1.2 m imaging flight tube.[62] The photofragment corresponding to the elimination of $C_3$ from each parent ion is selected via time-gating the detector. The spatial spread of ions resulting from KER is detected with an imaging detector (Beam Imaging Solutions), using methods described previously.[62−64] Images are accumulated with the NuAcq software[69,70] and calibrated using the photodissocation of $Ar_2^+$ with the same instrument settings.[63] The maximum KER value is determined from the outside edge of the image, at the point at which the signal rises above the baseline in the KER curve, with an additional downward correction for half of the resolution width of the instrument (determined by the line width of the signal for $Ar^+$ from dissociation of $Ar_2^+$ at these same instrument settings).[63] Computational studies were conducted using the Gaussian16 program package[71] at the DFT/B3LYP/def2-TZVP level of theory.

The mass spectrum of cluster cations produced by our source is shown in Figure S2. Figure 1 shows representative

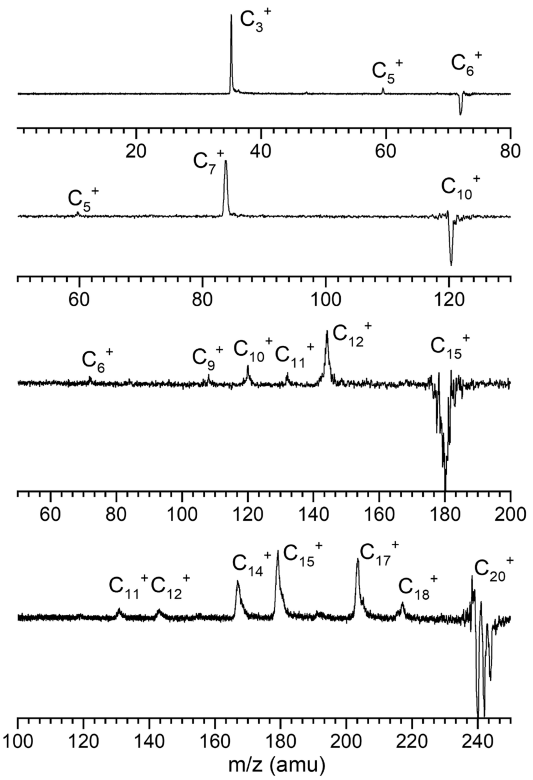


**Figure 1.** Photofragmentation mass spectra of selected carbon cluster cations at 355 nm. The data are collected with a difference method (photodissociation laser "on" − "off"). The depleted parent ion produces a negative signal, and the photofragments produce a positive signal.

examples of the photodissociation mass spectra of selected carbon ions that are relevant to this study. Additional fragmentation mass spectra are shown in Figure S3; Figures S4−S6 show the laser fluence dependence of the photodissociation for $C_{12}^+$, $C_{15}^+$, and $C_{20}^+$, respectively. The fragmentation mass spectra are collected with a difference method in which the intensity of the selected parent ion without laser excitation is subtracted from that of the mass spectrum with laser excitation that produces photofragments. The depletion of the parent ion is plotted in the negative direction, and the fragment ions produce a positive signal. The instrument is focused on the fragment masses, and the depletion of the parent ion is not representative of its actual intensity loss. As indicated, all of these cluster ions eliminate neutral $C_3$ as a prominent fragment, and in some cases, this is the only channel with significant intensity. It makes sense that


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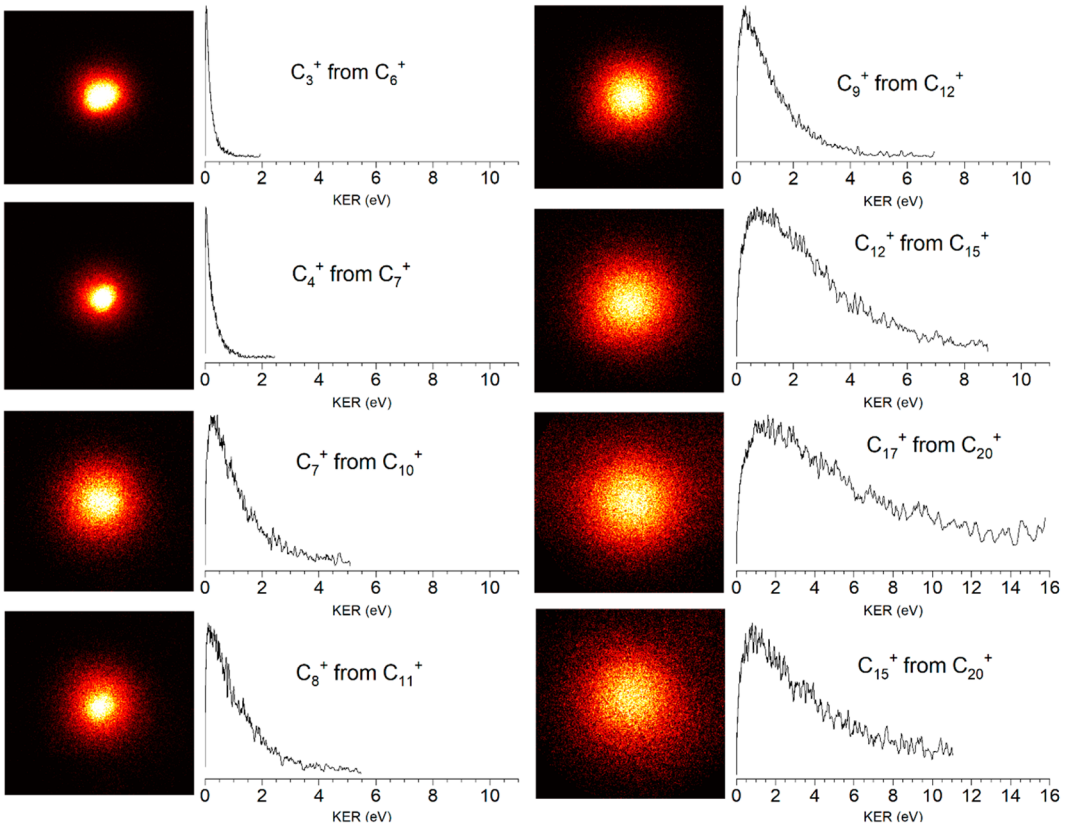


**Figure 2.** Photofragment images of carbon cluster cations ($C_n^+$) dissociated at 355 nm. In each case, the $n - 3$ cation is detected and imaged, except when $n = 20$, where the $n - 5$ fragment is also imaged.

$C_3$ is eliminated as a neutral because its ionization potential is higher than those of the larger fragments that retain the charge.[26] The larger clusters exhibit additional fragmentation channels corresponding to the loss of $C_2$ and $C_5$ neutrals. All of these fragmentation channels are consistent with those reported previously by other groups.[10−12,14,15,18] None of these fragmentation processes can be detected unless the photodissociation laser pulse energy is high (in the range of 15−40 mJ/cm$^2$), indicating that multiphoton absorption is likely causing the dissociation. The relative intensities of different fragment channels are roughly constant with the laser fluence (see Figures S4−S6).

Figure 2 shows the photofragment images for the $C_n^+$ clusters for $n$ = 6, 7, 10, 11, 12, 15, or 20, all using laser excitation at 355 nm. In each case, the image is for the $n - 3$ fragment ion, except in the case of $C_{20}^+$, where images for the $n - 3$ and $n - 5$ fragments are shown. Also shown are the kinetic energy spectra obtained by converting the velocity of the respective fragment ion into the total kinetic energy of both ion and neutral fragments. Although there is a distribution of kinetic energy for every cluster, and the most probable KER values are lower than the maximum values, each of these photodissociation processes produces a significant amount of kinetic energy release. The maximum KER ($KER_{max}$) values range from ∼1.0 eV for dissociation of $C_6^+$ and $C_7^+$ to 5−6 eV for $C_{15}^+$ and $C_{20}^+$. These images are isotropic, with significant amounts of intensity near their centers corresponding to low KER values, presumably resulting from the distribution of some fraction of the energy into internal rotational/vibrational/electronic states. Images were measured for selected cluster sizes with "slicing"[72] and produced no evidence for any anisotropy (see Figures S7 and S8). Because of this, and the much longer data collection times required for slicing, the images shown here were collected without slicing. However, all images indicate significant amounts of KER, and the amount increases for the larger clusters. Table 1 shows the dissociation energies determined from previous CID measurements[17] as well as a summary of the maximum $KER_{max}$ values measured for each cluster size. Although there is some uncertainty in the previous thermochemistry, there is no better information

**Table 1. Energetics of Carbon Cluster Cations (eV)**[a]

| | $D_0$ CID[17] | $KER_{max}$ | no. of photons/ excess energy | ring strain[76] |
|---|---|---|---|---|
| $l$-$C_6^+ \rightarrow C_3^+ + C_3$ | 5.2 | 0.8 | 2/1.71, 3/5.27 | n/a |
| $l$-$C_7^+ \rightarrow C_4^+ + C_3$ | 6.3 | 0.9 | 2/0.68, 3/4.17 | n/a |
| $c$-$C_{10}^+ \rightarrow C_7^+ + C_3$ | 5.9 | 2.8 | 2/1.08, 3/4.57 | 5.38 |
| $c$-$C_{11}^+ \rightarrow C_8^+ + C_3$ | 7.3 | 2.7 | 3/3.17 | 4.89 |
| $c$-$C_{12}^+ \rightarrow C_9^+ + C_3$ | 6.5 | 3.0 | 2/0.48, 3/3.97 | 4.48, 2.35[b] |
| $c$-$C_{15}^+ \rightarrow C_{12}^+ + C_3$ | 5.6 | 6.0 | 2/1.38, 3/4.87 | 3.59, 2.97[b] |
| $c$-$C_{20}^+ \rightarrow C_{17}^+ + C_3$ | – | 6.4 | 2/1.38, 3/4.87[c] | 2.69, 2.14[b] |
| $c$-$C_{20}^+ \rightarrow C_{15}^+ + C_5$ | – | 5.9 | 2/1.38, 3/4.87[c] | 2.69, 2.14[b] |

[a]Excess energies are for excitation with either two or three photons at 355 nm (3.49 eV). [b]This work, computed. [c]Estimated value assuming $D_0$ ($C_{20}^+$) = 5.6 eV (i.e., same as $C_{15}^+$).



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available. Considering the dissociation energies, the photon energies, and the KER values, these photodissociation processes likely represent multiphoton events involving two to four photons, and then a significant fraction of the excess energy results in KER.

Several additional experiments were performed to further investigate this photochemistry. Selected clusters were studied at different excitation wavelengths [355 nm vs 266 nm (Figures S9 and S10)] and as a function of the excitation laser fluence. Similar KER spectra were obtained under these conditions. As an example, Figure 3 shows the image of the $C_{15}^+$ cluster for

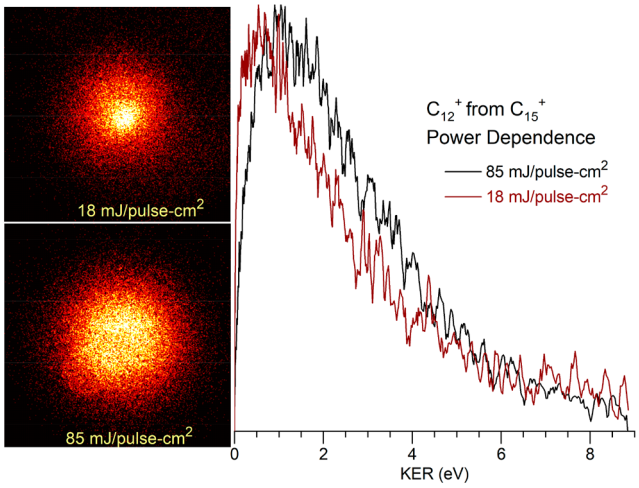


**Figure 3.** Photofragment images obtained for $C_{15}^+$ at laser pulse energies of 18 and 85 mJ pulse$^{-1}$ cm$^{-2}$.

photodissociation at 18 mJ pulse$^{-1}$ cm$^{-2}$ (the threshold for seeing the signal) and at 85 mJ pulse$^{-1}$ cm$^{-2}$. The signal intensities for these two experiments are very different, which affects the brightness of the image. Although the laser pulse energy is almost 5 times greater in the lower frame, the KER spectra are very similar. There is a slightly different position for the maximum in the signal at low energy, at roughly 1.0 eV versus 1.5 eV, but the KER values in both experiments extend to ~6 eV. This indicates that dissociation in both experiments is occurring at a similar high-energy state, but that the efficiency of reaching this state is greater with the higher laser pulse energy. This behavior is consistent with a multiphoton process, as suggested above.

Another issue is the temperature or internal energy of the carbon clusters. Because of their high bond energies, carbon clusters produced by laser vaporization are difficult to cool collisionally in supersonic expansions. Each addition of carbon to a growing cluster deposits the bond energy internally, heating the cluster, and the rate of collisional cooling may not be able to keep up with this in the finite time (a few microseconds) before ions expand into vacuum. If these carbon clusters are hot from their formation, this internal energy may contribute to the KER values detected. Different expansion gases (He/Ar mix and He/$N_2$ mix) were therefore used for cluster production, which should enhance the efficiency of collisional cooling (Figures S11−S13). Different growth channel lengths were also employed to increase the number of cooling collisions (Figure S14). None of these variables changed the KER detected by any significant amount. Therefore, although it is difficult to guarantee that these ions are internally cold, any residual internal energy apparently does not have a significant effect on the KER distributions. The KER values detected are primarily the result of the multiphoton photochemistry and dynamics.

Because of the multiphoton process, the exact excitation energy used in these photofragmentation events cannot be determined. However, some useful insight can be obtained from these data. Because $C_6^+$ and $C_7^+$ are linear and all of the other clusters here have cyclic structures, it is immediately apparent that the photodissociation of cyclic structures produces KER values greater than those for the dissociation of linear species. The $KER_{max}$ values for $C_{10}^+$−$C_{12}^+$ are 2−3 times greater than those for $C_6^+$ and $C_7^+$; the $KER_{max}$ values for $C_{15}^+$ and $C_{20}^+$ are 6 times greater than those for $C_6^+$ and $C_7^+$. This is surprising because all of the bond energies are roughly the same (5−7 eV according to previous CID experiments).[17] The much greater KER values for cyclic clusters suggests that either they are absorbing more photons or there is another source of energy contributing to the KER.

The energetics and KER values for the linear species $C_6^+$ and $C_7^+$ are similar. In both cases, the one-photon energy of the laser at 355 nm (3.49 eV) is significantly lower than the previously determined bond energies. This indicates that photodissociation requires at least two photons, but it may also involve more than two. Table 1 lists the excess energy that would be available for photodissociation following two- or three-photon absorption. If $C_6^+$ absorbs two photons, and the bond dissociation energy is 5.2 eV as determined from CID,[17] then there is 1.71 eV of excess energy deposited into the cluster. If the absorption involves three photons, the excess is 5.27 eV. Either of these scenarios provides enough excess energy to explain the 0.8 eV maximum value of the KER observed (i.e., $KER_{max}$), although two-photon absorption is more likely. In the case of $C_7^+$, two-photon absorption provides an excess energy of only 0.68 eV and three-photon absorption provides 4.57 eV. Unless the dissociation energy is lower than that determined previously, two-photon absorption does not provide enough excess energy to account for the 1.0 eV $KER_{max}$, but three-photon absorption does. A significant fraction of the available excess energy appears as KER instead of internal excitation.

In the case of $C_{10}^+$−$C_{12}^+$, the excess energies from two-photon absorption are not enough to account for the observed $KER_{max}$ values. In the case of $C_{11}^+$, the two-photon energy is not even great enough to dissociate the cluster. In each of these cases, at least three-photon absorption is required. The excess energy from three-photon absorption is then enough in each case to account for the $KER_{max}$ values. Again, however, a significant fraction of the available excess energy for each cluster would have to go into KER at the $KER_{max}$ energy (61% for $C_{10}^+$, 92% for $C_{11}^+$, and 65% for $C_{12}^+$). Considering this, it is conceivable that some four-photon absorption also contributes to these processes to account for the amount of KER. $C_{15}^+$ and $C_{20}^+$ each have the remarkable result of >6 eV of KER. The dissociation energy of $C_{20}^+$ has not been determined by CID experiments, but it is likely similar to the value for $C_{15}^+$. If this is true, then either two- or three-photon absorption is energetically sufficient to cause fragmentation, but at least four-photon absorption is required to explain the KER. The surprising result of all of these processes is that efficient multiphoton absorption is apparently required for dissociation and that much of the excess energy is converted into KER.



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Another factor possibly affecting these energetics is the steric strain present in the carbon clusters having ring structures ($n$ = 10, 11, 12, 15, or 20). The importance of ring structures in the early stages of fullerene growth has been documented.[73−76] The issue of ring strain has been discussed previously in the context of cluster dissociation during collisional excitation by Jarrold and co-workers.[76] Using a simple model and computed energetics, Jarrold estimated ring strain energies in the range of 3−5 eV for these clusters, with the greatest values for the smaller rings. Their estimates for ring strain energies are listed in Table 1. We have made similar estimates for selected cluster sizes with higher levels of theory, comparing the energies of broken-ring versus linear structures, and our numbers are also listed in Table 1. Although these estimates are approximate, the strain is significant, and it is greater for the smaller rings, varying from ∼5 eV for $C_{10}^+$ to just under 3 eV for $C_{20}^+$. Considering the mechanical recoil that occurs when a strained ring breaks, it is certainly possible that release of this strain could contribute to the KER. The ring strain energies are comparable to the photon energy of 3.49 eV at 355 nm. Therefore, if ring strain contributes to the KER values measured, the minimum number of absorbed photons required to explain the dynamics is smaller. The $KER_{max}$ values for $C_{10}^+$ and $C_{12}^+$ could be explained with a two-photon dissociation process. $C_{15}^+$ and $C_{20}^+$ both still require a process with at least three photons. The $C_{11}^+$ species is interesting, because the energy of two photons plus the ring strain would be enough to break the bond and explain the KER. However, it is not clear that ring strain could effectively couple to the system to enable bond breaking, as opposed to being released only after the bond breaks. If ring strain could influence the dissociation threshold, it would have affected the thresholds measured by CID. Therefore, release of ring strain only after bond breaking seems to be more plausible, and $C_{11}^+$ still requires a three-photon absorption for dissociation. If this is so, then the KER observed for this cluster size is a smaller fraction of the total available energy compared to other cluster sizes.

Because of the uncertainties in the number of photons absorbed and the role of ring strain, it is not possible to determine the exact energetics that produce the measured KER values for these carbon clusters. It is clear that photodissociation of the linear species $C_6^+$ can be explained with a two-photon process, with approximately half of the excess energy going into KER. $C_7^+$ requires a process with at least three photons, but with only ∼25% of the excess energy going into KER. $C_{10}^+$ and $C_{12}^+$ require three photons without any contribution from ring strain, but only two photons if there is a significant contribution from ring strain. The $C_{11}^+$ dynamics could be explained with the absorption of three photons, but only if essentially all of the excess energy goes into KER; this requirement is relaxed if there is a contribution from ring strain. $C_{15}^+$ and $C_{20}^+$ require either four-photon absorption or three-photon absorption and significant ring strain to explain their high KER values. It is then important to consider how such multiphoton processes are even possible. We have recently scanned the ultraviolet photodissociation excitation spectra of $C_{10}^+$ and $C_{12}^+$ and found that both of these ions have quasi-continuous spectra for wavelengths of <450 nm. If there are resonances at each photon step for these and the other carbon cluster ions, then the efficiency of multiphoton absorption is understandable.

The production of fragments with such high KER values is completely unexpected for these carbon cluster ions. High-energy photoexcitation of polyatomic molecules usually results in either prompt fluorescence or rapid nonradiative relaxation through internal conversion, intersystem crossing, and intramolecular vibrational relaxation (IVR). Significant internal redistribution of energy is therefore expected prior to bond breaking, and then only a small fraction of the total excess energy should be available for KER. KER usually becomes less likely statistically as the system size increases and the density of electronic and vibrational states increases. Fast photodissociation is possible in certain systems (e.g., organic carbonyls) where photoexcitation is localized on a specific active functional group. However, because of the symmetry of carbon clusters, electronic excitation should involve molecular orbitals delocalized over the molecular framework. KER is also enhanced if the excitation takes the system to the repulsive wall of an excited electronic state. However, it is extremely unlikely that this scenario would occur for all of the different sized carbon clusters studied here, or for those studied with excitation at different wavelengths. The production of high KER values and the increasing amount of this for the larger clusters are therefore quite surprising.

The best explanation for the photochemistry and dynamics here is that carbon cluster cations absorb multiple photons of ultraviolet light with high efficiency and that the energy absorbed is not converted effectively into the internal vibrational degrees of freedom. This is perhaps a consequence of the rigid structures and a poor coupling between electronic and vibrational states. This leads to significant kinetic energy release even for the linear structures, but substantially more for cyclic structures where ring strain can contribute to product ion recoil. However, ring strain alone does not completely account for the KER trend, as larger rings with less strain have even higher KER values. Another trend that may contribute is the lower dissociation energies for the larger clusters. The photochemistry must represent a strange mixture of efficient ultraviolet light absorption and dynamical conversion of the resulting energy into fragment recoil. It is conceivable that the initial fragmentation breaks one C−C bond, producing a highly excited "broken-ring" chain, and that a second step of fragmentation breaks a second C−C bond, eliminating the $C_3$ moiety. Additional energy could be gained by absorption of more photons by the broken ring or by its relaxed "uncoiled" form. However, if the ring is broken or even partially broken, the ring strain could not contribute effectively to KER. Relaxation to bending modes of the chain would likely be efficient. Linear structures do not produce high KER values when they dissociate, even when highly excited. Absorption of additional photons after partial fragmentation would likely show some dependence of the fragmentation channels or the KER on the photon energy or laser intensity, which we do not see. The simplest explanation consistent with all of the data is that multiphoton excitation produces a highly excited state where bond breaking occurs, that reaching this state is more efficient at higher laser powers, and that this superexcited species "shatters" or "explodes", undergoing simultaneous nonstatistical multifragmentation of two bonds, eliminating $C_3$. The ring strain is released in this event, contributing most effectively to the KER. The equally high KER for elimination of either $C_3$ or $C_5$ from $C_{20}^+$ would be consistent with this picture.

Unfortunately, it is difficult if not impossible to prove any mechanism such as this. Modeling these remarkable dynamics is completely intractable at present because of the size of these


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systems and the fact that the higher excited electronic states and vibrational frequencies of carbon cluster ions are largely unknown. Computations of dynamics in excited states would be confounded by the multireference character noted before. Electronic and vibrational spectroscopy experiments with these ions are ongoing, which together with excitation at different wavelengths to access different resonances, or perhaps two-color pump−probe experiments, may allow further insight into these fascinating dynamics.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c00950.

Full citation for ref 71 and the details of the DFT computations done, including the structures and energetics for each of the carbon cluster ions considered, mass spectra, fragmentation spectra, a figure of the imaging instrument, and images taken under different conditions (PDF)

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### Notes

The authors declare no competing financial interest.

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