

SMALL CARBON CLUSTERS ( $C_n^0$ ,  $C_n^+$ ,  $C_n^-$ ) FROM ACYCLIC AND CYCLIC  
PRECURSORS. NEUTRALIZATION-REIONIZATION MASS SPECTROMETRY  
AND THEORY

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**Abstract:** Ab initio calculations of isomeric carbon clusters  $C_n^0$  and  $C_n^+$ ,  $n = 2-4$ , yield structures and energies similar to previous reports, although five (not two)  $C_4^+$  structures have local energy minima. Dissociative ionization of structurally varied precursors was used to prepare  $C_3$  and  $C_4$  ionic and neutral isomers; however, their mass spectra from collisionally activated dissociation (CAD) and neutralization-reionization (NR) under a wide variety of conditions are indistinguishable, indicating only one isomer or the same mixture of isomers. Likewise, CAD and NR spectra of  $C_4^+$  and  $C_4^0$  from  $^{13}CH_2=CHCH=^{13}CH_2$  and  $C_3^+$  and  $C_3^0$  from  $CH_2=^{13}CHCH_3$  show complete  $^{13}C/^{12}C$  scrambling. CAD cross sections are consistent with  $C_4^+$  -  $C_6^+$  ions as mainly linear isomers and  $C_7^+$  ions from cyclic precursors as mainly cyclic. Product abundances from the unimolecular dissociation of  $C_n^0$ ,  $C_n^-$ , and  $C_n^+$  allow the selection of thermodynamic data that should be of higher relative accuracy, such as 11.4 eV for the  $C_3$  ionization energy from reported values of 10.0-13.0 eV.

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Carbon clusters were first studied spectroscopically using emission from interstellar clouds and other cosmic environments<sup>1,2</sup> and by mass spectrometry of carbon vapors.<sup>3</sup> As recently reviewed,<sup>4,5</sup> the chemistry of  $C_n$  molecules and ions in plasmas (carbon arcs, laser ablation)<sup>2-6</sup> and in the formation of polynuclear aromatics, diamond films,<sup>7</sup> and soot<sup>2,8</sup> has been the subject of extensive theoretical and experimental research. Of the latter, most studies have measured ionic species; in this study neutralization-reionization mass spectrometry (NRMS)<sup>9</sup> is used to investigate the isomers and energies of  $C_n^0$ , as well as  $C_n^+$  and  $C_n^-$ , clusters for  $n \leq 7$  by mass selection and neutralization of  $C_n^+$  ions from linear, branched, and cyclic molecules.

Theoretical calculations have predicted for small  $C_n^0$  species that odd-numbered clusters have lower electron affinities, closed shell ground states, and higher stabilities; for the cationic  $C_n^+$  counterparts, a similar order of stability was indicated, whereas for  $C_n^-$  anions an opposite trend was found.<sup>4,5,10-12</sup> Although stable  $C_n^0$  and  $C_n^+$  ( $n < 10$ ) structures were first predicted to be non-cyclic, more recent ab initio calculations show stability also for cyclic isomers,<sup>4,5,11</sup> with the two isomers close in energy for  $C_3^+$ ,<sup>11,13</sup>  $C_4^0$ ,<sup>11,14</sup> and  $C_4^+$ .<sup>11</sup>

In experimental studies, carbon vaporization, with and without postphotoionization, yields mass spectra with more abundant odd-numbered  $C_n^+$  and even-numbered  $C_n^-$  clusters,<sup>4,15-18</sup> as predicted by theory. This is more indicative of the relative stabilities of  $C_n^+$  and  $C_n^-$  than of  $C_n^0$ ; as pointed out for  $C_n^+$

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spectra by Bowers and co-workers,<sup>16</sup> the actual  $C_n^0$  abundances measured by mass spectrometry depend significantly on ionization cross sections and  $C_n^+$  stabilities. However, the high relative stability of  $C_3^0$  is supported by its preferential loss from both  $C_n^+$ <sup>4,16-18</sup> and  $C_n^-$ .<sup>15</sup> Mass-selected  $C_n^+$  clusters undergoing metastable,<sup>16</sup> collisionally activated,<sup>17,18a</sup> and laser dissociation<sup>4</sup> also favor formation of  $C_n^+$  species of odd-numbered  $n$  values.

Concerning isomeric characterization, evidence for open chain  $C_n^0$  and  $C_n^+$  has come from photoelectron,<sup>19</sup> infrared,<sup>20</sup> and microwave<sup>2,21</sup> spectroscopy, low energy  $C_n^+$  dissociations,<sup>16</sup> and ion mobility values.<sup>22</sup> However, stable cyclic structures are indicated for  $C_{4-6}^0$  neutrals and  $C_3^+$  ions by coulomb explosion techniques,<sup>23</sup> and, from the same laboratory, for  $C_3^0$  -  $C_7^0$  neutrals by electron affinity measurements;<sup>23c,24</sup> these values are much lower than those reported earlier,<sup>19</sup> possibly because the cyclic isomers are present in <10% concentration,<sup>23c</sup> with this value dependent on laser/graphite interaction conditions.<sup>24</sup> Additionally, cyclic  $C_5^+$  is indicated by infrared spectra using an argon matrix,<sup>25</sup> and a second, presumably cyclic,  $C_7^+$  isomer by differences in bimolecular reactivity<sup>18</sup> and ion mobility.<sup>22</sup> All of these studies utilized high-temperature formation from elemental carbon of these clusters, whose formation entropy should favor linear isomers.<sup>4</sup>

In a novel approach that could avoid this entropic preference, Lifshitz and co-workers<sup>17</sup> utilized dissociative

electron ionization of cyclic perchlorinated molecules to generate  $C_n^+$  with  $n = 3, 5, 6, 7$  and  $\geq 10$ , but found no evidence that this method gave different isomeric structures than those generated by carbon vaporization. Here we have extended this approach in an attempt to prepare linear, branched, and cyclic  $C_n^+$  ions;  $C_3^+$  and  $C_4^+$  have been studied the most extensively because their isomers are predicted to be stable and of closely similar energies.<sup>4,11,13,14</sup> Further, with NRMS<sup>9,26</sup> these mass-selected cations are then utilized to form the corresponding neutrals and anions. Product abundances from their competitive unimolecular dissociations are used to evaluate basic thermodynamic values proposed for  $C_n^0$ ,  $C_n^+$ , and  $C_n^-$  (Table I),<sup>4,5,27,28</sup> for which major disagreements still exist. Additional theoretical calculations have been carried out to guide these experiments.

## Experimental Section

Using a tandem double-focusing (EB-EB; E = electrostatic, B = magnetic sector) mass spectrometer described in detail elsewhere,<sup>29</sup> ions formed by 70-eV electrons are accelerated by 10 keV, mass selected by MS-I (EB), and undergo charge exchange collisions with a neutral target gas in a first collision cell (Cls-I) to form fast neutrals. The calcium neutralization experiments employed a special furnace for vaporization temperatures up to 800° C and special care to minimize Hg background (a reason that xenon was used as a high IE target

instead of Hg).<sup>29b</sup> Residual ions are deflected electrostatically, and the fast neutrals are made to undergo collisional reionization in Cls-II to yield cations or anions; negative ions are also formed by charge reversal of the precursor cations with C<sub>6</sub>H<sub>6</sub> in Cls-II. The resulting ions are mass separated in E-II and detected. For cross section values, the neutral beam flux is measured using a retractable channeltron multiplier at Cls-III before E-II. Following proposed conventions,<sup>30</sup> the designation <sup>+</sup>NR<sup>+</sup>, Na(85%T)/O<sub>2</sub>(70%T) indicates a spectrum from cation neutralization with Na at 85% precursor transmittance, followed by residual ion deflection (slash) and reionization to cations with O<sub>2</sub> at 70% transmittance. Data acquisition, reduction, and computer control employed a PC-based computer system.<sup>29c</sup>

Specific ion precursors included: hexabromobenzene (g-C<sub>6</sub>Br<sub>6</sub>), hexachlorobenzene (g-C<sub>6</sub>Cl<sub>6</sub>), benzene (g-C<sub>6</sub>H<sub>6</sub>), hexachlorocyclopentadiene (g-C<sub>5</sub>Cl<sub>6</sub>), 1,3-butadiene (n-C<sub>4</sub>H<sub>6</sub>), hexachloro-1,3-butadiene (n-C<sub>4</sub>Cl<sub>6</sub>), 1,4-dibromo-2-butyne (n-C<sub>4</sub>H<sub>4</sub>Br<sub>2</sub>), 1-bromo-2-methylpropene (i-C<sub>4</sub>H<sub>7</sub>Br), 1,2-dibromo-2-methylpropane (i-C<sub>4</sub>H<sub>8</sub>Br<sub>2</sub>), propene (n-C<sub>3</sub>H<sub>6</sub>), and cyclopropane (g-C<sub>3</sub>H<sub>6</sub>). H<sub>2</sub><sup>13</sup>C=CHCH=<sup>13</sup>CH<sub>2</sub> was synthesized adopting the procedure for the corresponding <sup>14</sup>C-isotopomer;<sup>31</sup> all other compounds, including CH<sub>2</sub>=<sup>13</sup>CHCH<sub>3</sub>, were obtained commercially.

**Theory.** Standard ab initio molecular orbital calculations<sup>32</sup> were carried out using the GAUSSIAN 88 program<sup>33</sup> with geometry optimizations at the HF/6-311G(d) level using the Quadratic Convergence technique (C<sub>2</sub><sup>+</sup> and C<sub>3</sub><sup>+</sup> structures were also optimized

at the UMP2/6-311(d) level). Harmonic vibrational frequencies were used both to characterize stationary points on the surface as minima (all frequencies real, representing equilibrium structures) or first-order saddle points (one imaginary frequency, representing transition structures), and (after scaling by 0.89) to calculate zero-point vibrational contributions to relative energies. Improved relative energies were obtained on the HF/6-311G(d) optimized geometries using Møller-Plesset perturbation theory (frozen core) terminated at second (MP2) and fourth (MP4) orders.

## Results and Discussion

**Theory.** Our ab initio calculations (Table II) were designed to search for new stable isomers to guide the experimental investigation. A broader exploration of the energy surface was sought here by utilizing a larger basis set, 6-311G(d). Ab initio calculations for carbon clusters are notoriously difficult and often require multi-configuration methods in order to obtain correct electronic states and isomer relative energies.<sup>4,5,10-14</sup> However, this was impractical in these extensive calculations, so that some stable isomers and electronic states were not identified. As found previously,<sup>13</sup> triplet excitations in the MP4 treatment exaggerate the relative stabilities of some isomers (Table II), but yield heats of atomization that are in better agreement with the experimental data and with previous calculations that include triple excitation.

Repeated optimizations of the  $C_2^+$  doublet found only the  $^2\Sigma_u^+$

state, while the multi-configuration calculations<sup>33</sup> find this as an excited state 275 kJ mol<sup>-1</sup> above the first  $a^2\Pi_u$  doublet state. Similarly, our  $C_2^+$  quartet state ( $^4\Pi_g$ ), bond length 1.222 Å, corresponds to the first excited state, 116 kJ mol<sup>-1</sup> above the previously identified  $X^4\Sigma_g^+$  ground state.<sup>33</sup> For the  $C_2^0$  neutral found previously,<sup>5,34</sup> the global minimum is the  $^1\Sigma_g^+$  state (bond length 1.24 Å), while the triplet corresponds to the  $c^3\Sigma_u^+$  excited state; the triplet-singlet energy difference (101 kJ mol<sup>-1</sup>) at MP4(SDQ) level is close to that published (113 kJ mol<sup>-1</sup>),<sup>33</sup> but the lowest triplet state ( $^3\Pi_u$ ) found previously<sup>4,5</sup> was not identified in our UHF geometry optimization. The cyclic  $^2B_2$   $C_3^+$  isomer has been found by many recent multi-configuration calculations<sup>14</sup> to be 8-25 kJ mol<sup>-1</sup> more stable than the linear  $^2\Sigma_u^+$ . We only find here the latter, a bent  $^2B_2$  isomer, and a linear quartet state as local minima. Neutral  $C_3$  calculations found the linear singlet ( $^1\Sigma_g^+$ ),<sup>5,35</sup> bond length 1.275 Å, and triplet ( $^3\Pi_u$ ) as ground and excited states, with an energy difference of 204 kJ mol<sup>-1</sup>, MP4(SDTQ), close to the calculated (197 kJ mol<sup>-1</sup>)<sup>36</sup> and experimental (203 kJ mol<sup>-1</sup>)<sup>37</sup> values.

Two stable  $C_4^+$  structures were identified previously by theory;<sup>4,11</sup> here an additional three were found as local energy minima (Table II and Figure 1). Of the species already identified,<sup>4,11</sup> we find the linear doublet  $1^+$  ( $^2\Sigma_u^+$ ) to be the most stable  $C_4^+$  species at the MP4(SDQ) level of theory, while the linear quartet  $3^+$  ( $^4B_g$ ) of a slightly distorted zigzag geometry

( $D_{\infty h} \rightarrow C_{2h}$ ) is the most stable isomer at MP4(SDTQ). The cyclic "A" quartet  $2^+$  is another stable structure of a slightly distorted rhombus geometry ( $D_{2h} \rightarrow C_s$ ). These distortions are likely artifacts of the UHF geometry optimization.<sup>34</sup> The calculated quartet states show significant spin contamination (Table II), suggesting the existence of other closely spaced high multiplicity states. Two other  $C_4^+$  species, the cyclic trapezoid  $4^+$  ( $^2A_2$  state) and the branched isomer  $5^+$  ( $^2B_1$  state), although significantly less stable, also represent minima, motivating our experimental search for further stable isomers.

Our calculations of the  $C_4$  neutral system (Table II) found no new isomers. Geometry optimizations led to the linear triplet, bond lengths 1.297 (end) and 1.274 Å, identified as the  $^3\Pi_g$  state, but not to the corresponding ground  $^3\Sigma_g^-$  state<sup>11-14</sup> lying 125-145 kJ mol<sup>-1</sup> below. We also found rhombic ( $^1A_g$ ) and linear ( $^1\Sigma_g^+$ ) singlet isomers, 138 and 20 kJ mol<sup>-1</sup> more stable than the triplet ( $^3\Pi_g$ ), at the MP4(SDQ) level of theory, consistent with previous calculations.<sup>14</sup> However, the linear singlet energy is too low in the MP4(SDTQ) calculations (Table II).

#### Isomer Characterization from CAD and NR Spectra.

Collisionally activated dissociation, CAD [ $O_2(50\%T)$ ] of 10 keV  $C_2^+$  -  $C_7^+$  clusters gave the Figure 2 spectra; the previously reported CAD (air) spectra of 8 keV  $C_3^+$ ,  $C_5^+$ ,  $C_6^+$ , and  $C_7^+$  ions are in agreement.<sup>17,18a</sup> However, our  $C_3^+$  and  $C_4^+$  spectra are independent ( $\pm 10\%$ ) of the wide variety of precursor molecules used. Further,

these spectra were not significantly changed by collisionally activating [He(50%T), first field-free region] the precursor ions to increase their average internal energy. The CAD spectra of  $C_6^+$  from  $\underline{c}$ - $C_6Cl_6$  and  $\underline{c}$ - $C_6Br_6$ , and of  $C_7^+$  from toluene and cycloheptatriene also were closely similar.

NR mass spectra have been used successfully to differentiate a multiplicity of isomers for cations whose CAD spectra are closely similar, such as those of  $C_4H_8$  and  $C_4H_4$ .<sup>38</sup> However, NRMS studies with the wide variety of  $C_n^+$  precursors (Figures 3,4) found no isomeric differences outside experimental error. The  $C_n^+$  charge exchange spectra [ $^+NR^-$   $C_6H_6$ (30%T), Figure 3] gave similar ( $\pm 20\%$ ) data for  $C_3^+$  and  $C_4^+$ , irrespective of the precursor used, and this was also true ( $\pm 10\%$ ) for neutralization of  $C_n^+$  with Xe, Na, or K followed by reionization [ $O_2$ (70%T), Figure 4].

All  $C_n^+$  spectra from xenon neutralization (70%T; IE = 12.1 eV) are dominated by the reionized precursor peak, with fragment peak abundances closely similar to those in the corresponding CAD spectra; this is consistent with the formation of these fragments by dissociation of cations after reionization, not by neutral dissociation.<sup>30</sup> More excited neutrals can be formed by using a target of lower ionization energy (IE), thus removing less energy from the ion in the neutralization process.<sup>9,26</sup> Using Na or K (IE = 5.1 or 4.3 eV) greatly reduced the reionized precursor peak for  $C_4 - C_8$  (Figure 4), consistent with a corresponding extent of neutral dissociation, but the fragment abundances were still independent ( $\pm 10\%$ ) of the precursor molecule used for all  $C_n^+$

ions studied.

The surviving precursor concentration from an intermediate extent of  $C_4^0$  dissociation should yield a more sensitive test of isomeric identity than the abundances of the  $C_{1-3}^0$  products, as dissociation could be preceded by isomerization of the  $C_4^0$  precursor. Neutralization with calcium (IE = 6.1 eV) did provide partial  $C_4^0$  dissociation (Table III), but  $^{+}NR^{+}$  spectra from five different precursors still had closely similar abundances of reionized  $C_4^{+}$  as well as  $C_{1-3}^{+}$  fragment ions.

As a further test of the stability of the linear isomer of  $C_4^{+}$  and  $C_4^0$ ,  $[1,4-^{13}C_2]-1,3$ -butadiene was used as a precursor in an attempt to generate  $^{13}C-^{12}C-^{12}C-^{13}C^{+}$ . Its CAD  $[O_2(70\%T)]$  and NR  $[K(90\%T)/O_2(70\%T)]$  spectra showed intensity ratios for  $m/z$  24:25:26 of 1.3:4.7:1 and 1.1:4.3:1, respectively, and ratios for  $m/z$  37:38 of 0.99:1 and 1.00:1, respectively. For these peak abundances, single bond dissociation of  $^{13}C^{12}C-^{12}C^{13}C$  without isomerization would yield 0:1:0 and 1:0, respectively; with complete scrambling, these ratios should be 1:4:1 and 1:1. Although isomerization is thus nearly complete, this does not necessarily indicate that the  $C_4^{+}$  ion is not linear or that the linear  $C_4^{+}$  ion is unstable, as isotopic scrambling could occur during formation of the  $C_4^{+}$  ion by dissociative ionization of the butadiene. Similarly, the CAD  $[He(70\%T)]$ , NR  $[K(90\%T)/O_2(70\%T)]$ , NR  $[K(90\%T)/He(70\%T)]$ , and charge reversal  $[C_6H_6(30\%T)]$  spectra of propene-2- $^{13}C$  also showed similar scrambling. The intensity ratios of  $m/z$  24:25 in these spectra were found to be 1:2.1,

1:2.0, 1:2.2, and 1:2.1, respectively; complete scrambling should give 1:2. Again, the  $C_3^+$  and/or  $C_3^0$  structures are not necessarily non-linear or unstable. However, all of the above data are consistent with the formation of both  $C_3^+$  and  $C_4^+$  from the various precursors as single isomers or similar mixtures of isomers.

**CAD and NR Efficiencies.** As reported earlier,<sup>4,16-18</sup> the relative yields of  $C_n^+$  in CAD spectra (Figure 2) are consistent with the expected higher stability of the odd-numbered cationic clusters. The relative efficiencies for CAD dissociation of  $C_n^+$  (Table IV) also reflect this stability relationship, assuming increasing dissociation cross section with increasing size, as found for metastable ion ( $\sim 10^{-5}$  s lifetime) dissociation.<sup>16,17</sup> Although mass discrimination<sup>39</sup> could affect the summed product cation abundances from CAD of  $C_n^+$ , the value for  $C_7^+$  is substantially below those of  $C_4^+$ ,  $C_5^+$ , and  $C_6^+$ . Metastable ion studies found a small<sup>17</sup> or significant<sup>16</sup> decrease in the cross section for  $C_7^+$  versus  $C_6^+$ , but still greater than the value for  $C_5^+$  ( $C_4^+$  was not measured). For ion-molecule reactions of laser-generated  $C_7^+$  ions, two-thirds were found to be unreactive with  $D_2$ , indicating that the majority of ions have the cyclic structure.<sup>18</sup> The relatively low degree of fragmentation for  $C_7^+ \rightarrow C_{<7}^+$  (Table IV) indicates that  $C_7^+$  is unusually stable and/or of smaller physical cross section for undergoing collision; either is consistent with a possibly higher fraction of cyclic isomers for  $C_7^+$  prepared by dissociative ionization of cyclic precursors.

As a corollary, this also implies that  $C_5^+$  and  $C_6^+$  are mainly the linear isomers. For the even-numbered, less stable  $C_4^+$  and  $C_6^+$  clusters, the increase in  $C_n^+ \rightarrow C_{<n}^+$  cross section values should be due primarily to increasing size, consistent also with a linear structure for  $C_4^+$ .

The  $C_n^+ \rightarrow C_{<n}^0$  neutralization efficiency (Table IV) decreases quite regularly from  $C_1$  (15.4%) to  $C_6$  (4.9%); the increasing physical cross section apparently is more effective in producing scattering than electron transfer. The  $C_n^0 \rightarrow C_{<n}^+$  reionization efficiency decreases even more dramatically from  $C_1$  (5.2%) to  $C_6$  (0.3%) despite decreasing IE values; neither the  $C_n^+ \rightarrow C_n^0$  nor  $C_n^0 \rightarrow C_n^+$  efficiencies reflect the odd/even nature of the cluster, consistent with the fact that odd clusters are more stable for both  $C_n^0$  and  $C_n^+$ . In contrast, the efficiency for forming  $C_n^-$  from  $C_n^+$ , as well as the <sup>stability</sup>  $C_n^- \rightarrow C_{<n}^-$  values, favors the even-numbered clusters, as expected. Although the efficiency for  $C_n^+ \rightarrow C_n^-$  drops substantially from  $C_2$  (0.90%) to  $C_6$  (0.14%), most of this appears to be due to the drop in neutralization efficiency,  $C_n^+ \rightarrow C_n^0$ ; the negative effect of size is far less for  $C_n^0 \rightarrow C_n^-$  than for the much higher energy  $C_n^0 \rightarrow C_n^+$  process.

**$C_n^0$  Heats of Formation ( $\Delta H_f$ ).** The  $\Delta H_f$  values of  $C_n^0$  from experimental and theoretical studies (Table I) were checked for their ability to predict competitive product abundances from unimolecular dissociations (Figure 4) after neutralization. This assumes minimal entropy requirements; energy release measurements for  $C_n^+$  metastable ion dissociations indicate negligible reverse

activation energy.<sup>16,17</sup> Comparisons can only be qualitative because of serious mass discrimination against smaller product ions. For example (Figure 4)  $[C_1^+]$ ,  $\Delta H_f = 717 \text{ kJ mol}^{-1}$ , in the  $C_3^+$  NR spectrum should even be higher than  $[C_2^+]$ ; the smaller  $C_n^0$  products have fewer vibrational degrees of freedom (none for  $C_1^0$ ), so that a higher proportion of excess excitation energy could become translational energy, increasing loss of the smaller product. Offsetting this somewhat, these do have higher reionization efficiencies (Table IV), and their abundances are also increased by secondary product dissociation, as shown by K versus Na neutralization.

For  $C_4^0$  NR data (Figure 4 and Table III), formation of  $C_1 + C_3$  is somewhat favored over that of  $2 C_2$ . Using  $\Delta H_f(C_1^0) = 717 \text{ kJ mol}^{-1}$  as the reference value,<sup>27</sup> the pairs of  $\Delta H_f(C_2^0, C_3^0)$  values (Table I) of (832, 837),<sup>27</sup> (815, 801),<sup>11a</sup> and (782, 773) predict that  $C_2^0$  formation is 110, 115, and 74  $\text{kJ mol}^{-1}$ , respectively, more endothermic than that of  $C_1^0 + C_3^0$ ; even the 74  $\text{kJ mol}^{-1}$  could be high. For  $C_5^0$  dissociation, using  $\Delta H_f(C_2^0, C_3^0)$  of 782 and 773 with  $\Delta H_f(C_4^0) = 971, 1022, \text{ and } 1012 \text{ kJ mol}^{-1}$  predicts endothermicities of 133, 184, and 174  $\text{kJ mol}^{-1}$  favoring the formation of  $C_2^0 + C_3^0$  over that of  $C_1^0 + C_4^0$ ; again the Figure 4 data would appear to favor the lowest value (the  $C_4^0$  reionization efficiency, Table IV, is half that of  $C_3^0$ ). For  $C_6^0$  dissociation using  $\Delta H_f(C_2^0, C_3^0, C_4^0)$  of 782, 773, and 971  $\text{kJ mol}^{-1}$  predicts an endothermicity of 207  $\text{kJ mol}^{-1}$  favoring formation of  $2 C_3^0$  over

that of  $C_2^0 + C_4^0$ ; this value appears more consistent with the Figure 4 data than those of 258 and 248  $\text{kJ mol}^{-1}$  derived with  $\Delta H_f(C_4^0) = 1022$  and  $1012 \text{ kJ mol}^{-1}$ . Using the  $\Delta H_f(C_5^0)$  values of 979 and  $1030 \text{ kJ mol}^{-1}$  with these  $\Delta H_f(C_2^0, C_4^0)$  values predicts endothermicities of 57 and 6  $\text{kJ mol}^{-1}$  favoring formation of  $C_1^0 + C_5^0$  over that of  $C_2^0 + C_4^0$ ; to agree with the Figure 4 data and subsequent correlations, 979  $\text{kJ mol}^{-1}$  has been chosen. These values, underlined in Table I, should be of higher relative accuracy than of absolute accuracy. These predict minimum energies of dissociation of  $C_2^0$ , 652;  $C_3^0$ , 726;  $C_4^0$ , 519;  $C_5^0$ , 576; and  $C_6^0$ , 343  $\text{kJ mol}^{-1}$ , consistent with higher stability for the odd-n-value neutral clusters.

$C_n^0$  Ionization Energies (IE). The agreement in reported IE values (Table I) is much poorer than even the accuracy presumed for our underlined  $\Delta H_f$  values. For example, the 10.4 to 13.0 eV values reported for IE ( $C_3^0$ ) are both substantially above, and substantially below, those of IE( $C_2^0$ ) and IE( $C_4^0$ ) (Table I). For this, comparison of the relative product yields in the NR and CAD spectra should be useful, as these should be affected mainly by the relative IE values, with mass discrimination at least qualitatively similar. Thus for the CAD spectrum of  $C_3^+ \rightarrow C_1^0 + C_2^+$  vs.  $C_2^0 + C_1^+$ , the 0.8 eV predicted lower IE of  $C_1^0$  should correspondingly favor  $C_1^+$  formation versus that of  $C_2^+$ , consistent with the CAD (Figure 2) versus NR (Figure 4) spectra of  $C_3^+$ . Comparing the CAD and NR spectra of  $C_4^+$ ,  $[C_3^+]/[C_1^+]$  and  $[C_3^0]/[C_1^0]$

are similar, suggesting comparable  $IE(C_3^0, C_1^0)$  values. The  $[C_3^+]/[C_2^+]$  yield is several times that of  $[C_3^0]/[C_2^0]$ , again in agreement with the lower  $IE(C_3^0)$  values found by theory, but not by other experiments (Table I); this is also borne out by the  $C_3/C_2$  values in the CAD and NR spectra of  $C_5^+$ . The  $C_5^+$  spectra also show that the  $[C_4^+]/[C_3^+]$  yield is somewhat greater than that of  $[C_4^0]/[C_3^0]$ , indicating  $IE(C_4^0) < IE(C_3^0)$ ; also consistent with this are the data of the  $C_6^+$  CAD and NR spectra. For the  $C_6^+$  spectra the  $[C_5^+]/[C_4^+]$  yield is somewhat greater than that of  $[C_5^0]/[C_4^0]$ , although this is offset by the poorer reionization efficiency of  $C_5^0$  vs.  $C_4^0$  (Table IV). Thus the IE values of  $C_1^0$  and  $C_3^0$  should be comparable, with  $C_2^0$  higher and  $C_4^0$  and  $C_5^0$  lower, consistent with the underlined values of Table I.

②  $\Delta H_f(C_n^+)$  Values. The heat of the formation values of the  $C_n^+$  species, which represent the sum of the  $\Delta H_f$  and IE values of the respective neutrals, can be used to predict the enthalpy differences in  $C_n^+$  dissociation products of the CAD spectra (Figure 2). The best agreement with these data, again recognizing mass discrimination, was obtained using the underlined  $\Delta H_f(C_n^+)$  values of Table I. From  $C_3^+$ , formation of  $C_2^+$  is predicted to be less favored by 82 kJ mol<sup>-1</sup>, but mass discrimination should greatly reduce  $[C_1^+]$ , which is still an abundant peak in the  $C_3^+$  CAD spectrum. From  $C_4^+$ ,  $C_1^+$  formation is 13 kJ mol<sup>-1</sup> favored over that of  $C_3^+$ , by far the most abundant peak, with  $C_2^+$  less favored by 156 kJ mol<sup>-1</sup>. From  $C_5^+$ ,

differential enthalpy values are  $C_4^+$ , 67;  $C_3^+$ , 0;  $C_2^+$ , 69, and  $C_1^+$ , 120 kJ mol<sup>-1</sup>; from  $C_6^+$ , these values are  $C_5^+$ , 84;  $C_4^+$ , 141;  $C_3^+$ , 0;  $C_2^+$ , 276; and  $C_1^+$ , 137 kJ mol<sup>-1</sup>; and from  $C_7^+$ , these values are  $C_6^+$ , 89;  $C_5^+$ , 17;  $C_4^+$ , 0;  $C_3^+$ , 66;  $C_2^+$ , 152; and  $C^+$ , 229 kJ mol<sup>-1</sup>. These values are qualitatively ( $\pm 30$  kJ mol<sup>-1</sup>) consistent with the Figure 2 spectra. These predict minimum energies of dissociation of  $C_2^+$ , 570;  $C_3^+$ , 713;  $C_4^+$ , 605;  $C_5^+$ , 642;  $C_6^+$ , 496; and  $C_7^+$ , ~777 kJ mol<sup>-1</sup>, consistent with higher stability for the odd-n-value cation clusters.

**NR Energy Deposition.** The differences between these  $\Delta H_f(C_n^+)$  values and the previous  $\Delta H_f(C_n^0)$  values yield  $IE(C_n^0)$  values (underlined, Table I) that can be checked further against the extent of  $C_n^0$  precursor dissociation in the  $\lambda$  spectra. The appropriate minimum internal energy  $E_{min}^*$  of  $C_n^0$  after neutralization is dependent on  $IE(C_n^0) - IE(\text{target})$ , with target  $IE(\text{Mg, Na, K}) = 6.1, 5.1, \text{ and } 4.3$  eV. As an example,<sup>39</sup> neutralization of  $CH_4^+$  ( $IE = 12.5$  eV) with K should produce  $CH_4^0$  with  $E_{min}^* = 12.5 - 4.3 = 8.2$  eV. The product yields are  $CH_4^+$ , 0%;  $CH_3^+$ , 53%; and  $CH_2^+$ ,  $CH^+$ , and  $C^+$ ; 47%. This results from dissociation thresholds of 4.6 eV for  $CH_4^+$  and 9.3 eV for  $CH_3^+$ ,<sup>27</sup> 1.1 eV above  $E_{min}^*$ .

The neutralization of  $C_3^+$  by Na (K) should produce  $C_3^0$  with  $E_{min}^* = 6.3$  (7.1) eV; this causes 53% (75%)  $C_3^0$  dissociation that requires 7.5 eV, or 1.2 (0.4) eV above  $E_{min}^*$ . Neutralization of  $C_4^+$  by Mg (Na) should produce  $E_{min}^*(C_4^0) = 4.6$  (5.6) eV; this causes

59% (94%)  $C_4^0$  dissociation that requires 5.4 eV, or 0.8 eV above (0.2 eV below)  $E_{\min}^*$ . Neutralization of  $C_5^+$  by Mg (Na) should produce  $E_{\min}^*(C_5^0) = 4.6$  (5.6) eV; this causes 28% (69%)  $C_5^0$  dissociation that requires 5.8 eV, or 1.4 (0.4) eV above  $E_{\min}^*$ . Neutralization of  $C_6^+$  by Mg (Na) should produce  $E_{\min}^*(C_6^0) = 3.7$  (4.7) eV; this causes 75% (96%) dissociation that requires 3.6 eV or 0.1 (1.1) eV below  $E_{\min}^*$ . The agreement of these data with each other, and with that of  $CH_4$ , is  $\sim \pm 0.3$  eV. An exception is  $C_2^0$ , which is only 32% dissociated. The excited electronic states of the small  $C_2^0$  molecule should have well separated intersystem crossings, and thus some could have sufficiently long lifetimes ( $> 0.5 \mu s$ ) to reach the reionization cell before dissociation.

**$\Delta H_f(C_n^-)$  Values.** Such an evaluation for the negative ions can be made using the charge exchange  $^+NR^-$  spectra of Figure 3. With the underlined values of Table I, all dissociations are predicted to be highly endothermic (850 kJ mol $^{-1}$  for  $C_2^-$ ), consistent with Figure 3. From  $C_3^-$  the formation of  $C_2^-$  is predicted to be favored by 198 kJ mol $^{-1}$ . From  $C_4^-$ , differential enthalpy values are  $C_3^-$ , 58;  $C_2^-$ , 0; and  $C_1^-$ , 124 kJ mol $^{-1}$ . From  $C_5^-$ , these values are  $C_4^-$ , 96;  $C_3^-$ , 132;  $C_2^-$ , 0; and  $C_1^-$ , 331 kJ mol $^{-1}$ . From  $C_6^-$ , these values are  $C_5^-$ , 68;  $C_4^-$ , 38;  $C_3^-$ , 0;  $C_2^-$ , 75; and  $C_1^-$ , 216 kJ mol $^{-1}$ . Eyler has recently reported<sup>28</sup> electron affinities for  $C_4^0$ ,  $C_5^0$ , and  $C_6^0$  of 1.3 - 1.5 eV, far lower than those derived from the Table I values. Note that dissociation channels other

than those accompanied with  $C_3$  neutral loss are also prominent, contrary to the photofragmentation results.<sup>18</sup> These  $\Delta H_f(C_n^-)$  values predict minimum energies of dissociation of  $C_2^-$ , 850;  $C_3^-$ , 594;  $C_4^-$ , 630;  $C_5^-$ , 526; and  $C_6^-$ , 551 kJ mol<sup>-1</sup>, consistent with higher stability for the even-n-value anion clusters.

### Conclusions

Although multiple isomeric  $C_3^0$  and  $C_4^0$  species are predicted to be stable, those prepared from a wide variety of linear, branched, and cyclic (and isotopically labeled) precursors give NR spectra indicative of only one isomer, presumably the linear one. Consistent with results from gas-phase ion chromatography,<sup>16</sup> CAD cross sections indicate that  $C_5^+$  and  $C_6^+$  are also linear, but that  $C_7^+$  is cyclic. Values of  $\Delta H_f(C_n^0, C_n^+, C_n^-)$  and  $IE(C_n^0)$  selected from previous experimental and theoretical studies, plus from calculations here, can be fit to reaction enthalpies consistent with these NR and CAD spectra, indicating values that should be of improved relative accuracy.

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Table I. Heats of Formation (298 K, kJ mol<sup>-1</sup>) and Ionization Energies (eV); chosen values underlined.

| Species                              | $\Delta H_f(C_n^0)$    | IE                      | $\Delta H_f(C_n^+)$     | $\Delta H_f(C_n^-)^a$ |
|--------------------------------------|------------------------|-------------------------|-------------------------|-----------------------|
| C <sub>1</sub> expt <sup>b</sup>     | <u>717</u>             | 11.3                    | <u>1803</u>             | <u>595</u>            |
| theory <sup>d</sup>                  | 717 <sup>c</sup>       | 11.0                    | 1778                    |                       |
| theory <sup>e</sup>                  | 717 <sup>c</sup>       | 11.1                    | 1788                    |                       |
| C <sub>2</sub> expt <sup>b,f</sup>   | 832                    | 12.1                    | 1998                    | 505                   |
| theory <sup>d</sup>                  | 815 <sup>g</sup>       | 12.1                    | 1983                    | 497                   |
| theory <sup>e,g</sup>                | <u>782</u>             | <u>12.1</u>             | <u>1950<sup>e</sup></u> | <u>462</u>            |
| C <sub>3</sub> expt <sup>b</sup>     | 837                    | 12.1                    | 2004                    | 649                   |
| expt <sup>h</sup>                    |                        | 13.0                    |                         |                       |
| theory                               | 801 <sup>d</sup>       | <u>11.4<sup>d</sup></u> | <u>1872<sup>g</sup></u> | 613                   |
| theory <sup>e</sup>                  | <u>773</u>             | 10.4                    | 1776                    | 585                   |
| C <sub>4</sub> expt <sup>b</sup>     | <u>971</u>             | 12.6 <sup>b,h</sup>     | 2187                    | <u>614</u>            |
| expt <sup>g</sup>                    |                        | <u>10.7</u>             | <u>2004</u>             |                       |
| theory <sup>d</sup>                  | 1022                   | 10.5                    | 2033                    | 665                   |
| theory <sup>e</sup>                  | 1012                   | 11.3                    | 2102                    | 655                   |
| C <sub>5</sub> expt                  | <u>979<sup>i</sup></u> | 11.5 <sup>i</sup>       | 2024                    | <u>709</u>            |
| expt                                 |                        | 12.3 <sup>h</sup>       | <u>2012<sup>g</sup></u> |                       |
| theory <sup>d</sup>                  | 1030                   | <u>10.7</u>             | 2066                    | 760                   |
| C <sub>6</sub> expt                  | $\geq 1180^k$          | 9.6 <sup>i</sup>        | $\geq 2106^i$           | $> 784$               |
| expt <sup>h</sup>                    |                        | 9.7                     |                         |                       |
| theory <sup>d,1</sup>                | 1203                   | 9.8                     | <u>2149</u>             | <u>807</u>            |
| $\underline{c}$ -C <sub>7</sub> expt | $\geq 1146^k$          |                         | $\geq 1923^l$           | $\geq 847$            |
| theory <sup>d</sup>                  | $< 1263^m$             |                         | $< 2073^n$              | $< 964$               |
| $\underline{n}$ -C <sub>7</sub> expt | $>> 1146^{k,m}$        |                         | $>> 2111^{m,o}$         | $>> 847$              |
| theory <sup>d</sup>                  | 1263 <sup>m</sup>      |                         | 2227 <sup>p</sup>       | 964                   |

Footnotes for Table I.

<sup>a</sup>Using  $\Delta H_f(C_n^0)$  plus vertical electron affinity (EA) values from ref. 19 except EA(C<sub>1</sub>) from ref. 27; EA(C<sub>3</sub>-C<sub>6</sub>) from ref. 12 are lower by 28-40 kJ mol<sup>-1</sup>. <sup>b</sup>From ref. 27. <sup>c</sup>Reference value used in the theoretical calculations. <sup>d</sup>Calculated from data (total electronic energy, fundamental frequencies, IE, etc.) of ref. 11a, with thermal corrections and heat of atomization (binding energy, 0 K) scaled by 1.1. <sup>e</sup>As in d from our calculations at the MP4 (STDQ) level; IE(C<sub>2</sub><sup>0</sup>) from the total energy of the C<sub>2</sub><sup>+</sup> quartet state, corrected by the excitation energy  $E(^4\Pi_g) - E(^4\Sigma_g^-) = 1.2$  eV from the MCSF-SCEP calculations, ref. 42; C<sub>4</sub> calculated for the rhombus structure. <sup>f</sup>Experimental value of 815 kJ mol<sup>-1</sup> from Urdahl, R.S.; Bao, Y.; Jackson, W.M. Chem. Phys. Lett. **1991**, 178, 425-428. <sup>g</sup>From the present experimental data and the underlined IE values. <sup>h</sup>From ref. 28. <sup>i</sup>From ref. 18c. <sup>j</sup>Chase, M. W.; Davies, C. A.; Downery, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. J. Phys. Chem. Ref. Data **1985**, 14, Supplement 1: JANAF Thermochemical Tables, Third Edition. <sup>k</sup>Drowart, J.; Burns, R. P.; Demaria, G.; Inghram, M. G. J. Chem. Phys. **1959**, 31, 1131-1132. <sup>l</sup>Linear isomer (ref. 11a). <sup>m</sup>Assuming the cyclic isomer to be the more stable. <sup>n</sup>Using the theoretical IE value from ref. 18c. <sup>o</sup>Ref. 28; IE(linear) - IE(cyclic) = 1.6 eV from theory and 1.9 eV from experiment. <sup>p</sup>Using the IE value from Koopman's theorem.

Table II . Calculated total energies of carbon cluster ions and neutrals.

| Ion/<br>Neutral                                                          | $\langle S^2 \rangle^b$ | total energy <sup>a</sup> |             |             |             | ZPVE <sup>c</sup> |
|--------------------------------------------------------------------------|-------------------------|---------------------------|-------------|-------------|-------------|-------------------|
|                                                                          |                         | SCF                       | MP2         | MP4(SDQ)    | MP4(SDTQ)   |                   |
| C ( <sup>1</sup> P)                                                      | 0                       | -37.598730                | -37.669305  | -37.694076  | -37.694885  |                   |
| C ( <sup>3</sup> P)                                                      | 2.01                    | -37.689049                | -37.745023  | -37.763780  | -37.764302  |                   |
| C <sub>2</sub> ( <sup>1</sup> $\Sigma_g^+$ )                             | 0                       | -75.393686                | -75.718201  | -75.720480  | -75.757361  | 11.4              |
| C <sub>2</sub> ( <sup>3</sup> $\Sigma_u^+$ )                             | 2.01                    | -75.465389                | -75.665165  | -75.681075  | -75.691228  | 14.3              |
| C <sub>3</sub> ( <sup>1</sup> $\Sigma_g^+$ )                             | 0                       | -113.378370               | -113.726307 | -113.743722 | -113.776683 | 23.2              |
| C <sub>3</sub> ( <sup>3</sup> $\Pi_u$ )                                  | 2.21                    | -113.283383               | -113.645172 | -113.659625 | -113.697914 | 20.0              |
| C <sub>4</sub> ( <sup>1</sup> $\Sigma_g^+$ )                             | 0                       | -151.166223               | -151.758917 | -151.628814 | -151.859454 | 41.9              |
| C <sub>4</sub> ( <sup>3</sup> $\Pi_g$ )                                  | 2.28                    | -151.214780               | -151.618959 | -151.620997 | -151.677634 | 42.4              |
| C <sub>4</sub> ( <sup>1</sup> A <sub>g</sub> )                           | 0                       | -151.175999               | -151.659151 | -151.673560 | -151.708357 | 35.3              |
| C <sup>+</sup> ( <sup>2</sup> P)                                         | 0.76                    | -37.291796                | -37.336540  | -37.357692  | -37.358019  |                   |
| C <sup>+</sup> ( <sup>4</sup> P)                                         | 3.75                    | -37.158039                | -37.167617  | -37.170724  | -37.170734  |                   |
| C <sub>2</sub> <sup>2+</sup> ( <sup>2</sup> $\Sigma_u^+$ ) <sup>d</sup>  | 0.80                    | -74.922290                | -75.161871  | -75.170107  | -75.188772  | 13.8              |
| C <sub>2</sub> <sup>+</sup> ( <sup>4</sup> $\Pi_g$ )                     | 3.75                    | -75.093854                | -75.242087  | -75.262514  | -75.268205  | 13.2              |
| C <sub>3</sub> <sup>+</sup> ( <sup>2</sup> B <sub>2</sub> ) <sup>e</sup> | 0.85                    | -112.938031               | -113.301503 | -113.311787 | -113.343776 | 23.4              |
| C <sub>3</sub> <sup>+</sup> ( <sup>2</sup> B <sub>2</sub> ) <sup>d</sup> | 0.85                    | -112.936514               | -113.303785 | -113.310393 | -113.350904 |                   |
| C <sub>3</sub> <sup>+</sup> ( <sup>2</sup> $\Sigma_u^+$ ) <sup>f</sup>   | 0.78                    | -112.910338               | -113.321953 | -113.315460 | -113.388621 | 22.5              |
| C <sub>3</sub> <sup>+</sup> ( <sup>2</sup> $\Sigma_u^+$ ) <sup>d</sup>   | 0.78                    | -112.908702               | -113.323758 | -113.317587 | -113.394710 |                   |
| C <sub>3</sub> <sup>+</sup> <sup>g</sup>                                 | 3.99                    | -112.977334               | -113.231845 | -113.255894 | -113.272173 | 23.1              |
| C <sub>4</sub> <sup>+</sup> ( <sup>2</sup> $\Sigma_u^+$ )                | 0.89                    | -150.828454               | -151.237934 | -151.280966 | -151.307179 | 32.2              |
| C <sub>4</sub> <sup>+</sup> ( <sup>4</sup> B <sub>g</sub> )              | 4.14                    | -150.776199               | -151.237982 | -151.264185 | -151.308558 | 36.2              |
| C <sub>4</sub> <sup>+</sup> ( <sup>2</sup> A <sub>2</sub> )              | 2.67                    | -150.814654               | -151.181499 | -151.219405 | -151.240990 | 35.1              |
| C <sub>4</sub> <sup>+</sup> ( <sup>4</sup> A'')                          | 3.86                    | -150.831167               | -151.246165 | -151.265529 | -151.293238 | 36.1              |
| C <sub>4</sub> <sup>+</sup> ( <sup>2</sup> B <sub>1</sub> )              | 1.37                    | -150.731486               | -151.100270 | -151.150165 | -151.173292 | 27.3              |

Footnotes for Table II .

<sup>a</sup>Geometry optimizations and energy calculations with the 6-311G(d) basis set, energy in hartrees.

<sup>b</sup>Spin contamination value (ref. 40).

<sup>c</sup>Zero point vibrational energy from 6-311G(d) harmonic frequencies, unscaled, kJ mol<sup>-1</sup>.

<sup>d</sup>Geometries optimized at the UMP2/6-311G(d) level.

<sup>e</sup>First-order saddle point, single imaginary frequency.

<sup>f</sup>Second-order saddle point, two degenerate imaginary frequencies.

<sup>g</sup>Quartet, state unassigned.

Table III.  $^{+}NR^{+}$  Spectra of  $C_4^{+}$ , Ca( $\sim 85\%T$ )<sup>a</sup>/ $O_2$ ( $70\%T$ ).

| Precursor                                | <u>m/z</u> | 12 | 24 | 36 | 48 |
|------------------------------------------|------------|----|----|----|----|
| <u>n</u> -C <sub>4</sub> H <sub>6</sub>  |            | 5  | 16 | 56 | 23 |
| <u>n</u> -C <sub>4</sub> Cl <sub>6</sub> |            | 6  | 16 | 60 | 19 |
| <u>c</u> -C <sub>5</sub> Cl <sub>6</sub> |            | 6  | 14 | 60 | 21 |
| <u>c</u> -C <sub>6</sub> H <sub>6</sub>  |            | 5  | 19 | 56 | 19 |
| <u>c</u> -C <sub>6</sub> Cl <sub>6</sub> |            | 7  | 17 | 58 | 18 |

<sup>a</sup>Transmittance from 690°C Ca vaporization.

Table IV. Cross Sections for CAD and NR Spectra.

| Cluster | $C_n^+{}^a$<br>$\rightarrow C_{\leq n}^+$ | $C_n^+{}^b$<br>$\rightarrow C_{\leq n}^0$ | $C_n^+{}^c$<br>$\rightarrow C_{\leq n}^-$ | $C_n^0{}^d$<br>$\rightarrow C_{\leq n}^+$ | $C_n^-{}^e$<br>$\rightarrow C_{\leq n}^-$ |
|---------|-------------------------------------------|-------------------------------------------|-------------------------------------------|-------------------------------------------|-------------------------------------------|
| $C_1$   | -                                         | 15.4                                      | 0.40                                      | 5.2                                       | -                                         |
| $C_2$   | 0.28                                      | 12.6                                      | 0.90                                      | 2.1                                       | <1                                        |
| $C_3$   | 0.42                                      | 9.8                                       | 0.23                                      | 1.8                                       | 18                                        |
| $C_4$   | 1.8                                       | 7.7                                       | 0.24                                      | 0.90                                      | 25                                        |
| $C_5$   | 1.8                                       | 6.3                                       | 0.09                                      | 0.60                                      | 37                                        |
| $C_6$   | 2.8                                       | 4.9                                       | 0.14                                      | 0.30                                      | 20                                        |
| $C_7$   | 0.80                                      | -                                         | -                                         | -                                         | -                                         |

${}^a C_n^+$  CAD,  $O_2(50\%T)$ , efficiency: total  $C_n^+$  product ion abundance, in % of unattenuated precursor ion abundance ( $\pm 20\%$  relative).  ${}^b C_n^+$  neutralization,  $Xe(70\%T)$ , efficiency: total  $C_{\leq n}^0$  flux, % of unattenuated precursor ion abundance ( $\pm 10\%$  relative).  ${}^c C_n^+$  charge reversal,  $C_6H_6(30\%T)$ , efficiency: total  $C_{\leq n}^-$  abundances, % of unattenuated precursor abundance ( $\pm 20\%$  relative).  ${}^d C_n^0$  [from  $Xe(70\%T)$  neutralization of  $C_n^+$ ] reionization,  $O_2(70\%T)$ , efficiency: total  $C_{\leq n}^+$  abundances, % of total  $C_{\leq n}^0$  flux ( $\pm 20\%$  relative).  ${}^e C_{\leq n}^-$  dissociation efficiency in charge reversal spectra,  $C_6H_6(30\%T)$ : total  $C_{\leq n}^-$  product ion abundance, % of survival  $C_n^-$ .

### Figure Legends

- Figure 1** Calculated geometries of  $C_4^+$ :  $\underline{1}^+$ ,  ${}^2\Sigma_u^+(D_{\infty h})$ ;  $\underline{2}^+$ ,  ${}^4A''(D_{2h} \rightarrow C_s)$ ;  $\underline{3}^+$ ,  ${}^4B_g(D_{\infty h} \rightarrow C_{2h})$ ;  $\underline{4}^+$ ,  ${}^2A_2(C_{2v})$ ;  $\underline{5}^+$ ,  ${}^2B_1(C_{2v})$ . Bond lengths are in Angstroms.
- Figure 2** CAD spectra,  $O_2(50\%T)$ , identical ( $\pm 10\%$ ) for the same ion from the listed precursors: (A)  $C_2^+$  from  $n-C_3H_6$ ,  $n-C_4Cl_6$ ; (B)  $C_3^+$  from  $n-C_3H_6$ ,  $n-C_4Cl_6$ ,  $\underline{c}-C_3H_6$ ,  $\underline{c}-C_5Cl_6$ ; (C)  $C_4^+$  from  $n-C_4H_6$ ,  $n-C_4H_4Br_2$ ,  $n-C_4Cl_6$ ,  $\underline{i}-C_4H_8$ ,  $\underline{i}-C_4H_7Br$ ,  $\underline{i}-C_4H_8Br_2$ ,  $\underline{c}-C_5Cl_6$ ,  $\underline{c}-C_6H_6$ , and  $\underline{c}-C_6Cl_6$ ; (D)  $C_5^+$  from  $\underline{c}-C_5Cl_6$ ; (E)  $C_6^+$  from  $\underline{c}-C_6Cl_6$  and  $\underline{c}-C_6Br_6$ ; and (F)  $C_7^+$  from toluene and cycloheptatriene.
- Figure 3** Charge reversal  ${}^+NR^-$  spectra,  $C_6H_6(30\%T)$ , identical ( $\pm 20\%$ ) for the same ion from the listed precursors: (A-F)  $C_1^+-C_6^+$ , respectively, as in Figure 2, except  $C_4^+$  is from  $n-C_4Cl_6$ ,  $\underline{i}-C_4H_7Br$ , and  $\underline{c}-C_5Cl_6$ . Higher trace is amplified tenfold.
- Figure 4**  ${}^+NR^+$  spectra,  $Y/O_2(70\%T)$ , identical ( $\pm 10\%$ ) for the same ion from the listed precursors: (A)  $C_1^+$ , (B,G,L)  $C_2^+$ , (C,H,M)  $C_3^+$ , (D,J,N)  $C_4^+$ , (E,J,O)  $C_5^+$ , (F,K,P)  $C_6^+$ , with (A-F)  $Y = Xe(70\%T)$ , (G-K)  $Y = Na(85\%T)$ , (L-P)  $Y = K(90\%T)$ . Precursors as in Figure 2, except  $C_3^+$  is from  $n-C_3H_6$  and  $n-C_4Cl_6$  and also from  $\underline{c}-C_3H_6$  and  $\underline{c}-C_5Cl_6$  with K neutralization;  $C_4^+$  is from  $n-C_4Cl_6$ ,  $\underline{i}-C_4H_7Br$ , and  $\underline{c}-C_5Cl_6$  and also from  $\underline{c}-C_6Cl_6$  with Na and K neutralization. Numeric values for precursors are the % of the value with no collisions (value for Mg neutralization in parenthesis.) Product values are relative peak areas, corrected for dissociation after reionization indicated in the Xe spectra, averaged for the multiple measurements.

Figure 1







