Small Carbon Clusters: Spectroscopy, Structure, and Energetics

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I. Introduction

The study of pure carbon molecules has engaged great interest for many decades. Molecules of this kind were first detected in astrophysical sources over a century ago and continue to be intensely studied in connection with the chemistry of carbon stars, comets, and interstellar molecular clouds. In particular, long carbon chains have recently been proposed as possible carriers of the diffuse interstellar bands. Carbon clusters are known to be present in hydrocarbon flames and other soot-forming systems, and the study of these species is necessary for acquiring a thorough understanding of these complex chemical environments. Carbon clusters are also thought to be intermediates in the gas-phase chemistry taking place in chemical vapor deposition systems for production of thin diamond and silicon carbide films. Clearly, a detailed knowledge of the physical and chemical properties of carbon clusters is important for understanding a large variety of chemical systems.

In addition to such practical considerations, carbon clusters are fascinating examples of the richness and variety of carbon chemistry in itself. Due to the enormous bonding flexibility of carbon, viz. its unique ability to form stable single, double, or triple bonds, carbon clusters appear in a wide range of structural forms that are synthesized spontaneously in hot carbon plasmas. For example, researchers have been puzzling for more than a decade over the ability of a molecule as symmetric as the icosahedral C_{60} cluster to form in such a spontaneous way. Elucidating the evolution of carbon cluster structure, from linear chains to rings to closed spheroidal cages to nanotubes, that takes place as the cluster size increases constitutes a major scientific challenge and requires an intimate interplay of state of the art experimental and theoretical techniques. While great progress has been made in recent years, many unanswered questions still remain.

The enormous volume of carbon cluster research that occurred prior to 1989 was the subject of a comprehensive review article by Weltner and Van Zee. In the years since the publication of that review, an explosion in carbon cluster research has occurred. The ability to efficiently synthesize C_{60}, C_{70}, and other fullerene species in bulk quantities has spawned a new branch of chemistry, which was recently recognized with the Nobel Prize. Many researchers from around the world have contributed to a vast and expanding literature on the physical and chemical properties of this third stable allotrope of carbon. New nanoscale materials have also been discovered as an outgrowth of this research, e.g. the so-called “buckytubes” and much effort has been expended in developing technological applications for these species. Recent research on fullerenes and nanotubes is the subject of numerous books and review articles. See for example, refs 23–27.

Prior to the 1985 discovery of fullerenes, the existence of a stable sp allotrope of carbon, composed of long acetylenic chains of sp-hybridized carbon atoms (polyynes) was proposed. Carbon chains, such as HC₃N, possessing as many as 11 carbon atoms, had been observed in the interstellar medium and evidence for the existence of even larger species of this kind was obtained from laboratory measurements. In more recent years, Lagow et al.
succeeded in synthesizing bulk quantities of such carbon chains containing as many as 28 carbon atoms by stabilizing the terminal carbons with bulky organic end-capping groups. These authors also reported evidence for gas-phase carbon chains produced with as many as 300 atoms. On the basis of these observations, they suggested that long chains of sp-hybridized carbon atoms may constitute a "fourth stable allotrope of carbon".

sp carbon molecules in their pure form are known to exist in a rich variety of structures, including chains and monocyclic and polycyclic rings. These molecules are highly reactive, transient species and are extremely difficult to produce and study in the laboratory. Nevertheless, great progress has been made in the study of these systems since the publication of Weltner and Van Zee's review, especially for clusters in the C_3 to C_20 size range. In particular, very little detailed experimental information that could directly elucidate the structural properties of polyatomic carbon clusters larger than C_3 existed prior to 1989. This situation has largely been rectified in more recent years, especially for the linear isomers of C_4, C_7, C_9, and C_13, for which extremely precise high-resolution infrared laser spectroscopy experiments have been performed. Many other spectroscopic techniques have also been developed to study carbon molecules in the gas phase and trapped in cryogenic matrices. For example, new experimental and theoretical studies of the optical spectra of C_3 have led to a much more detailed understanding of the unusual bending dynamics of this molecule. In addition, vibrationally resolved photoelectron spectroscopy has been used to characterize numerous vibrational and electronic states of gas-phase clusters up to C_{11}. The study of carbon clusters trapped in cryogenic matrices is a continuing area of active research. In recent years, numerous infrared absorption bands observed in matrices have been assigned, through the interplay of isotopic substitution measurements, ab initio calculations, and subsequent gas-phase measurements. Very recently, two infrared absorption transitions observed in an Ar matrix have been assigned to vibrational modes of the elusive cyclic isomers of C_6 and C_8.

Much of this recent experimental progress has been devoted to characterizing carbon clusters in their ground electronic states, and traditionally, much less has been known about the excited electronic states of clusters larger than C_3. However, beginning in 1995, there has been a recent flurry of activity in this area. A significant new development in the field of matrix spectroscopy is the ability to trap mass-selected carbon cluster anions in solid matrices. Optical emission and absorption spectroscopy measurements have been performed for both the anionic and neutral forms of mass-selected linear carbon chains ranging in size from C_4 to C_{20}, leading to unambiguous assignments of numerous electronic transitions. Many of these transitions have also been observed recently for the anionic carbon clusters in the gas phase, using multiphoton electron detachment techniques.

Another area of carbon cluster research that has been notoriously difficult to address has been to obtain structural information about carbon clusters in the intermediate size range between small chains and rings and large closed-cage fullerene species. It was recently discovered that much could be learned about carbon cluster ions in this size range by measuring their ion mobilities using gas-phase ion chromatography. Structural properties, isomer distributions, and relative energies have been elucidated in detail for cluster ions as small as C_6 and as large as C_{84} in this way. Finally, much more accurate measurements of electron affinities, ionization potentials, and dissociation energies for carbon clusters as large as C_{24} are now available.

Many of the issues discussed above are being addressed by applying new theoretical methods to increasingly larger carbon clusters, including fullerenes. For example, powerful coupled cluster techniques, which have become widely available only in the past few years, have now been used to calculate the properties of carbon clusters as large as C_{10} with unprecedented accuracy. Recent improvements in density functional theory methods have also permitted more accurate ab initio calculations to be carried out for clusters as large as C_{20}. Clearly, much new insight now exists, and the purpose of the present article will be to review this recent progress. Weltner and Van Zee's review covered a time period that extended back to the earliest days of carbon cluster research in the 1940s and 1950s, up until the time of publication in 1989. This paper will concentrate on recent developments that have taken place since that time. The main focus will be on the structural, spectroscopic, and energetic properties of pure sp carbon clusters and their ions in the C_2 to C_{30} size range.

II. Structure, Bonding, and Vibrational Dynamics

A. Geometric Structures

Ever since the pioneering molecular orbital calculations of Pitzer and Clementi, it has been recognized that carbon clusters smaller than C_{10} possess low-energy linear structures. Cumulenic bonding (:C=...C=C::), with nearly equivalent bond lengths, as opposed to acetylenic bonding, (:C==C...C==C::) with alternating bond lengths, was predicted to be the preferred bonding configuration. Odd-numbered linear chains were thought to possess Σ_g^+ ground electronic states, whereas the ground states were Σ_g^− for the even-numbered chains. Clusters larger than C_{10} were believed to occur as monocyclic rings, due to the reduction in angle strain of the larger rings and the added stability arising from an additional C–C bond. For the most part, these early predictions have been vindicated by sophisticated ab initio calculations, at least in a qualitative sense. Linear chains are indeed low-energy isomeric forms for the smaller clusters, and a transition to rings is still thought to occur at C_{10}. In addition, the acetylenic configurations of the even-numbered linear chains are found to be higher in energy than the cumulenic forms, although there is evidence that...
the energy separation between the two forms reduces as the length of the chain increases. At the CISD/DZP level of theory, for example, the cumulenic form of C4 was 33 kcal/mol more stable than the acetylenic structure, while for linear C10 the energy difference was only 4.9 kcal/mol at this level. Recent evidence from density functional theory has shown that the ground-state planar monocyclic ring isomers of C8, C12, and C16 may actually be polyacetylenic structures.

In more recent years, a major caveat to the early molecular orbital calculations was discovered. For the even-numbered clusters, C4, C6, and C8, cyclic isomers were also found to be low-energy structures and are now thought to be isoenergetic to or lower in energy than their linear counterparts. The ground-state planar monocyclic ring isomers of C8, C12, and C16 may actually be polyacetylenic structures.

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As stated above, the ground states are of \(1\Sigma_g^+\) and \(3\Sigma_g^+\) character for the odd- and even-numbered clusters, respectively. Among the physical properties that are most sensitive to the nature of the electronic states are the electron affinities (EA's), the ionization potentials (IP's), and the dissociation energies (DE's). Measurements of these properties provide, for example, experimental support for the alternation between singlet and triplet electronic states for odd-numbered linear chains. The latest experimental and theoretical values for EA's and IP's are plotted in Figure 2a,b. DE's for the most favorable dissociation channels of carbon cluster cations are plotted in Figure 2c. A similar even-odd alteration...
of DE's for C_{3}-C_{9} is expected to occur for the neutral species as well.

UV photoelectron spectroscopy measurements of mass selected C_n^- ions (3 ≤ n ≤ 84) were first used to determine EA's. The EA's of C_{2}-C_{9} alternated between larger values for n-even and smaller values for n-odd, consistent with the predicted spin multiplicity of the linear chains. An abrupt decrease in the electron affinity was observed for C_{10}, which was taken as support for a transition to monocyclic rings. More precise values for the EA's of C_{2}-C_{11} were later obtained by Arnold et al. using vibrationally resolved photoelectron spectroscopy techniques.

Estimates for the IP's of carbon clusters were first provided by Rohlfing et al. on the basis of laser photoionization measurements of the neutrals, More recent measurements have been made using the charge-transfer bracketing technique wherein recent measurements have been made using the results for clusters smaller than C_{10}. In general, these calculations are in reasonable agreement with the experimental carbon clusters. In general, these calculations are in reasonable agreement with the experimental carbon clusters.

Finally, Radi et al. and Sowa-Resat et al. performed collision-induced dissociation measurements to determine the dissociation behavior of C_n^- (2 ≤ n ≤ 19). For C_{2}^- to C_{4}^-, the lowest energy dissociation channel was the loss of C^+. Loss of C_{3}^- was the lowest energy channel for C_{5}^- to C_{9}^-.

These clusters are often observed as "magic number" peaks in photoionization mass spectra. The unusual abundance of these clusters may thus be due to their low IP's rather than to a special degree of stability.

III. Formation of Carbon Clusters

Carbon clusters form spontaneously in plasmas that are produced during the energetic processing of carbon-rich materials. Such natural environments include the atmospheres surrounding carbon stars, interstellar dust clouds irradiated by intense UV light, and terrestrial sooting flames. The most widely used laboratory technique for producing carbon clusters has been laser vaporization of graphite followed by supersonic expansion into an inert carrier gas, usually He or Ar. Smalley and co-workers first developed this technique, which was employed by Kroto et al. in the discovery of fullerenes. Neutral, anionic, and cationic carbon clusters form directly from the laser initiated plasma in sizes ranging from one to hundreds of atoms. The size distribution and the isomorphic forms produced in this way can be controlled by varying such experimental parameters as laser power, gas pressure, and the geometry of the supersonic nozzle. Magic number peaks sometimes are observed in the mass spectra of smaller C_n^- ions for odd-numbered clusters, especially n = 3, 11, 15, and 19. In contrast, for small C_n^- ions, magic
number peaks have been observed to occur for even-numbered clusters.92,93 Measurement of the neutral carbon cluster distribution produced by laser vaporization of graphite has been hindered by the lack of a "soft" ionization technique, wherein the neutrals are ionized without fragmentation. Recently, Kaizu et al. used single photon (10.5 eV) ionization of the neutrals, as opposed to previously reported multiphoton ionization, to obtain a reliable measurement of the neutral cluster size distribution (see Figure 4).94 These authors found that, under moderate vaporization laser fluences (0.1–1.0 J/cm²), magic number peaks occurred at n = 10, 12, 14, 16, and 18, analogous to the anion distribution. In contrast, the size distribution observed after multiphoton ionization at 3.5 eV revealed the familiar bimodal distribution33 dominated by odd-numbered peaks in the lower mass range and even-numbered fullerenes in the higher mass range. The authors concluded that under these conditions, the neutrals were produced predominantly as even numbered monocyclic rings, and that formation of the anions proceeded by electron capture of the neutrals.

The use of laser vaporization—supersonic expansion sources continues to be an important means of producing carbon clusters for their study in the gas phase. Laser vaporization of thin diamond films and organic polymers has also been used to produce carbon clusters,95–97 as has laser vaporization of a metal target in the presence of small hydrocarbons seeded into the carrier gas.98 Other methods of producing carbon clusters that do not involve laser vaporization include the carbon arc synthesis of macroscopic quantities of fullerenes and nanotubes,22 electric discharge, photolysis, or pyrolysis of small hydrocarbon precursors,89,99–102 CO₂ laser vibrational activation of SF₆ in the presence of acetylene,103 and Cs ion sputtering of graphite.104 Diederich and co-workers105–109 and others110 have been developing techniques to systematically synthesize specific sized carbon clusters from organic precursors. They have shown, for example, that C₁₈ can be produced by photolyzing an 18-membered cyclic carbon ring stabilized by organic leaving groups.106

Although most of the techniques mentioned above involve synthesis and characterization of carbon clusters in the gas phase, major contributions to carbon cluster research have been made by trapping the clusters in cryogenic matrices and measuring UV/vis, infrared, and ESR spectra.1,46,111 Larger carbon clusters are built up from smaller precursors by annealing the solid matrix. Early matrix studies by Weltner and co-workers date back to the 1960s, but advances continue to be made, due to the availability of more sophisticated theoretical methods for predicting vibrational frequencies and isotope substitution patterns for assigning infrared spectra. Rare gas matrices are typically used, although solid para-hydrogen has recently been shown to give higher resolution IR spectra.112 Figure 5 displays a recent IR absorption spectrum of carbon clusters trapped in an Ar matrix.113 While many of the peaks have been assigned to fundamental vibrational transitions of different sized carbon clusters, numerous unas-
signed transitions still remain. Analysis of these data is complicated by the fact that a broad distribution of cluster sizes is present in the matrix, and several regions of the spectrum are too congested to perform reliable isotopic substitution measurements. This weakness is currently being overcome by depositing mass-selected carbon cluster anions into the matrix, followed by electron photodetachment to form the neutral.46 Another difficulty is that the matrix environment may perturb the structure and spectral properties of the molecules being studied, as will be shown in several cases below. As will soon become clear, most of the assignments that have been made have been accomplished in recent years, through a combination of isotopic substitution measurements, ab initio calculations, and gas-phase infrared laser spectroscopy.

IV. Thermodynamic Properties

A long-standing problem in studying the physical properties of graphite has been to determine an accurate value for the heat of vaporization. Complexity arises due to the large distribution of clusters present in the equilibrium vapor, and it becomes necessary to determine accurate heats of formation for each individual carbon cluster. This problem has been investigated in recent years on both experimental114–116 and theoretical117,118 grounds.

Gingerich et al. used Knudsen effusion mass spectrometry to measure the equilibrium partial pressures of the C2—C7 carbon clusters in graphite vapor at temperatures ranging from 2660 to 2850 K.114–116 Of the pure carbon species present in the vapor, C1, C2, and C3 accounted for nearly all of the total vapor pressure. C3 was the major component, accounting for about 80% of the vapor pressure at 2700 K, while C1 and C2 were present at about 14% and 6%, respectively. The larger clusters (C4—C7) existed only in trace quantities at these temperatures, accounting for less than 0.1% of the pure carbon species. Molecular partition functions were calculated within the rigid rotor—harmonic oscillator approximation using experimental and theoretical spectroscopic data. From the partial pressure data and the calculated partition functions, the authors deduced thermodynamic properties, including third law heats of formation, $\Delta H^\circ$, and total atomization energies, $\Sigma D_0$, for linear C2—C7. Martin and Taylor recently calculated $\Sigma D_0$ values for C2—C10 using coupled cluster methods.118 Table 1 compares their results to the experimental values.

Two weaknesses exist in deducing $\Delta H^\circ$ and $\Sigma D_0$ values from the vapor pressure measurements. The first, and most serious, is the assumption of a rigid rotor—harmonic oscillator model in the third law extrapolations, since large anharmonicities are present in the bending modes of the linear systems, especially for C3 and C7. A second weakness is that the authors assumed only the linear isomers to be present for the even-numbered C4 and C6 clusters, even though cyclic isomers are predicted to be present as well. However, it has been shown that due to the higher density of states of the linear isomers, resulting from their lower bending frequencies, these species possess higher entropies of formation.119,120 Thus, the linear isomers may be formed more readily at temperatures attained in the partial pressure measurements, as well as for laser vaporization conditions, even when the cyclic species are lower in energy. For example, Slanina estimated that the rhombic isomer of C4 would account for no more than 10% of the C4 clusters present in the vapor at equilibrium, based on theoretical calculations.120 In a similar study, the percentage of cyclic C6 was found to be only 3% at 2500 K.119 Therefore, the assumption that only linear isomers are present under these conditions is probably a reasonable one to make.

V. C2

A. Structure and Spectroscopy

As discussed above, C, C2, and C3 are the primary components of equilibrium carbon vapor at temperatures in the range of 2000–5000 K. These species are reaction intermediates in a wide variety of chemical systems involving hydrocarbons, including photolysis, electric discharges, and combustion systems. The largest fraction of the carbon present in the universe is in the form of C or one of its ions, while the molecular form of CO accounts for the second largest fraction. C2 and C3 are also present in astrophysical sources and are thought to be important reactants in the chemistry of the interstellar medium. The spectroscopy of these species has been studied for decades, making C2 and C3 by far the most well-characterized of all the carbon clusters. In fact, one author recently described C3 as “one of the most well-characterized nonrigid triatomics in existence”.121

The C2 molecule exists in a $X^1\Sigma^+$ ground electronic state. There are three low lying electronic states that have also been characterized, the $a^3\Pi_u$ state, lying 716 cm$^{-1}$ above the ground state, the $b^3\Sigma_u^+$ state at 6434 cm$^{-1}$, and the $A^1\Pi_u$ state at 8391 cm$^{-1}$. In addition to these low-lying states, about 14 other electronic states have been observed giving rise to a rich spectroscopy. Since C2 is most often produced in an emissive state, many well-known band systems have been characterized. The most prominent of

<table>
<thead>
<tr>
<th>C2</th>
<th>$\Delta H^\circ$ (kcal/mol)</th>
<th>$\Sigma D_0$ (kcal/mol)</th>
<th>C3</th>
<th>$\Delta H^\circ$ (kcal/mol)</th>
<th>$\Sigma D_0$ (kcal/mol)</th>
<th>C4</th>
<th>$\Delta H^\circ$ (kcal/mol)</th>
<th>$\Sigma D_0$ (kcal/mol)</th>
<th>C5</th>
<th>$\Delta H^\circ$ (kcal/mol)</th>
<th>$\Sigma D_0$ (kcal/mol)</th>
<th>C6</th>
<th>$\Delta H^\circ$ (kcal/mol)</th>
<th>$\Sigma D_0$ (kcal/mol)</th>
<th>C7</th>
<th>$\Delta H^\circ$ (kcal/mol)</th>
<th>$\Sigma D_0$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>195(2)</td>
<td>144(2)</td>
<td>C3</td>
<td>199(3)</td>
<td>311(3)</td>
<td>C4</td>
<td>251(4)</td>
<td>429(4)</td>
<td>C5</td>
<td>258(4)</td>
<td>592(4)</td>
<td>C6</td>
<td>314(4)</td>
<td>706(5)</td>
<td>C7</td>
<td>317(4)</td>
<td>873(5)</td>
</tr>
</tbody>
</table>

$^a$ Numbers in parentheses are uncertainties in the last digits. $^b$ References 114–116. $^c$ References 117 and 118.
these is the Swan system (d$^2\Pi_g$→a$^3\Pi_u$) at ~19 400 cm$^{-1}$. Others include the Phillips bands (A$^2\Pi_u$→X$^1\Sigma^+_g$) and the Mulliken bands (D$^1\Sigma^+_u$→X$^1\Sigma^+_g$) at 43 227 cm$^{-1}$. The most recent states to be characterized were the B$^1\Delta_g$ and B$^3\Sigma^+_g$ states, which were detected by Douay et al. via the B$^1\Delta_g$→A$^2\Pi_u$ and the B$^3\Sigma^+_g$→A$^2\Pi_u$ infrared emission spectra of a hydrocarbon discharge.122 and the 1$^1\Delta_g$ state, observed by Goodwin and Cool via the 1$^1\Delta_g$→A$^2\Pi_u$ transition.123 Gong et al. have recently measured radiative lifetimes of several vibronic states of C$_2$(B$^3\Sigma^+_g$).124 The structural and spectroscopic properties of C$_2$ known prior to 1977 were tabulated by Huber and Herzberg.125 Experimental and theoretical studies up to 1989 were summarized in Weltner and Van Zee’s review article.1 Finally, Martin reviewed the spectroscopy and kinetics of all the C$_2$ electronic states studied up to 1992.126 Calculated and experimental molecular constants, vibronic frequencies, excited-state lifetimes, oscillator strengths, and electronic transition moments for most of the observed electronic states are reported in these references.

Experimental and theoretical work on C$_2$ since 1992 has mostly aimed at refining and improving the accuracy of the calculated properties and the measured molecular parameters and resolving a few discrepancies that existed in the earlier work. Watts and Bartlett calculated equilibrium bond lengths, harmonic vibrational frequencies, dissociation energies, and the electronic term energies for C$_2$ in its X$^1\Sigma^+_g$, a$^2\Pi_u$, and b$^2\Sigma^+_g$ states.127 One of the purposes of this study was to provide a benchmark for extending coupled cluster techniques to larger carbon clusters. Various coupled cluster techniques using different methods for treating triple excitations were compared. Although the most accurate of these was the full CCSDT approach, the CCSD(T) method was found to be the best compromise between accuracy and cost. The most accurate calculations were performed using the cc-pVQZ basis set. Pradhan et al. used multireference configuration interaction methods to obtain the ground-state spectroscopic constants of C$_2$.128 Various basis sets were compared, the largest one being the cc-pV6Z basis set.

The Swan system of C$_2$ was recently studied by Prasad and Bernath using Fourier transform spectroscopy of C$_2$ molecules cooled in a supersonic jet.129 These authors reported refined values for the molecular constants of V$^\prime$ = 0→4 and V$^\prime$ = 0→3. The “high-pressure band system” is observed as an enhancement of the V = 6 level population within the Swan system that takes place in CO discharges as well as a variety of other experimental conditions. Tharjæ and Ablasha observed high-pressure bands in a laser produced carbon plasma and concluded that the bands resulted from the recombination of ground-state carbon atoms.130 Caubet and Dorthe attempted to elucidate the origin of the high-pressure bands produced in a microwave discharge of CO.131 Previously, it was suggested that the enhancement results from collisional transfer between the metastable $^3\Pi_g$ state and d$^2\Pi_g$, ν = 6. These authors found that population of the $^3\Pi_g$ resulted from the reactions C + C + M → C$_2$ + M and C + C + O → C$_2$ + CO.

### Table 2. Molecular Parameters of the D$^3\Sigma^+_u$ (ν′ = 0) State of C$_2$ab

<table>
<thead>
<tr>
<th>band</th>
<th>$v_0$ (cm$^{-1}$)</th>
<th>B$_g$ (cm$^{-1}$)</th>
<th>D$_g$ (×10$^6$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0→0</td>
<td>43227.33(40)</td>
<td>1.82322(15)</td>
<td>7.39(29)</td>
</tr>
<tr>
<td>1→1</td>
<td>43209.31(33)</td>
<td>1.80370(39)</td>
<td>7.29(20)</td>
</tr>
<tr>
<td>2→2</td>
<td>43175.77(23)</td>
<td>1.78390(06)</td>
<td>7.19(30)</td>
</tr>
<tr>
<td>3→3</td>
<td>43151.14(25)</td>
<td>1.76470(50)</td>
<td>7.09(35)</td>
</tr>
<tr>
<td>4→4</td>
<td>43121.92(15)</td>
<td>1.74724(20)</td>
<td>7.6(20)</td>
</tr>
</tbody>
</table>

a Adapted from ref 135. b Numbers in parentheses are uncertainties in the last digits.

One of the discrepancies that had existed between experiment and theory was the value of the oscillator strength of the Phillips System. Experimental measurements were consistently lower than the theoretical calculations. A new value for f$^A_{0→1}A^0$ was recently deduced by Lambert et al., on the basis of astrophysical observations using the Hubble Space Telescope, that was in better agreement with theory.132 Erman and Iwamae re-measured radiative lifetimes of the Phillips system and determined a value for f$^A_{0→1}A^0$ of (1.36 ± 0.15) × 10$^{-3}$, which is compared to the astrophysical estimate of (1.23 ± 0.16) × 10$^{-3}$ and the theoretical value of 1.45 × 10$^{-3}$.133 Lask et al. studied the Phillips bands of $^{13}$C$_2$ and $^{12}$C$_2$ trapped in Ne and Ar matrices by laser induced fluorescence.134 They found that radiationless intersystem crossing efficiently populates the a$^2\Pi_u$ and b$^2\Pi_g$ states upon excitation of the Phillips bands, while the d$^2\Pi_g$ state was populated by two-photon absorption, permitting the observation of the Swan bands.

The Mulliken bands were first observed in 1930, and the molecular constants determined in 1939.126 No other measurement of the molecular constants were reported until the laser induced fluorescence study of Blunt et al., who determined revised values for the D$^3\Sigma^+_u$ state.135 Table 2 displays selected molecular constants for the Mulliken band recently obtained by these authors.

### B. C$_2$−

Production of neutral carbon clusters is often accompanied by the formation of carbon cluster ions. Although the relative abundances of these ions is usually much lower than those of the neutrals, their high chemical reactivity makes them important components in the growth and annealing of carbon clusters. C$_2$− is the most well-characterized of all the carbon cluster ions. This molecule is particularly interesting because it possesses valence electronic states that are bound with respect to electron auto-detachment. The most sophisticated theoretical study to be performed on C$_2$− to date is the coupled cluster (CCSDT) calculations of Watts and Bartlett.127 These authors calculated the equilibrium bond length, the vibrational frequency, the dissociation energy, and molecular constants for the X$^2\Sigma^+_g$ ground state and the B$^1\Sigma^+_g$ and A$^2\Pi_u$ excited states. High-resolution gas-phase spectroscopy has been used to characterize the B$^1\Sigma^+_g$→X$^2\Sigma^+_g$ and the A$^2\Pi_u$→X$^2\Sigma^+_g$ transitions providing molecular constants, oscillator strengths, and excited-state lifetimes. More recently, de Beer et al. used stimulated Raman pumping to characterize C$_2$−.137
Table 3. Molecular Parameters of the \( \chi^{2}\Sigma_{g} (\nu' = 0) \) and the \( \chi^{2}\Sigma_{u} (\nu = 1) \) State of \( \text{C}_2 \)^{1,2,3}

<table>
<thead>
<tr>
<th>parameter</th>
<th>( \chi^{2}\Sigma_{g} )</th>
<th>( \chi^{2}\Sigma_{u} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_v ) (cm(^{-1}))</td>
<td>0.0</td>
<td>21213.1958(90)</td>
</tr>
<tr>
<td>( B_v ) (cm(^{-1}))</td>
<td>1.41786(7)</td>
<td>1.52234(9)</td>
</tr>
<tr>
<td>( D_v ) (10(^{-6}) cm(^{-1}))</td>
<td>6.32(10)</td>
<td>6.46(13)</td>
</tr>
<tr>
<td>( \gamma_v ) (10(^{-4}) cm(^{-1}))</td>
<td>-</td>
<td>-4.00(20)</td>
</tr>
<tr>
<td>( \epsilon_v ) (10(^{-2}) cm(^{-1}))</td>
<td>4.2(11)</td>
<td>5.4(5)</td>
</tr>
</tbody>
</table>

\(^{a}\) Adapted from ref. 141. \(^{b}\) Numbers in parentheses are uncertainties in the last digits. \(^{c}\) The parameters of the \( B \) state were obtained from analysis of the spin–orbit interaction between the \( B \) state and the close-lying (2)\( \Pi \) state. \(^{d}\) Spin–rotation coupling constant. \(^{e}\) Spin–spin coupling constant.

Resonant two-photon photodetachment (R2PD), via transitions to the \( 2\Sigma_{u}^{+} \) state, followed by detection of the zero kinetic energy (ZEKE) electrons, was used to monitor the ground-state population as a function of Stokes frequency.

C. \( \text{C}_2^{+} \)

The \( \text{C}_2^{+} \) ion was considerably more difficult to characterize using high-resolution spectroscopy techniques than \( \text{C}_2 \), and a complete picture of its spectroscopic properties has emerged only recently. \( \text{C}_2^{+} \) was first observed in the gas-phase with rotational resolution by Maier and Rösslein, who analyzed vibronic bands in the \( \chi^{2}\Sigma_{u}^{+}-\chi^{2}\Sigma_{g}^{+} \) system.\(^{138}\) Later, Celii and Maier used stimulated emission pumping (SEP) spectroscopy to access higher excited vibrational states (\( \nu = 4 \rightarrow 6 \)) in the \( \chi^{2}\Sigma_{u}^{+} \) ground state.\(^{139}\) The resolution of the rotational lines was about 0.3 cm\(^{-1}\). Carré et al. studied the (1,0) transition of the \( \chi^{2}\Sigma_{u}^{+}-\chi^{2}\Sigma_{g}^{+} \) spectrum using fast-ion beam laser spectroscopy.\(^{140}\) Rather than tuning the laser over the transition, laser induced fluorescence signals were observed by Doppler scanning the transition into resonance with a fixed-frequency laser. Using this technique, the authors observed the rovibronic transitions with line widths of 0.004 cm\(^{-1}\). With this large improvement in the resolution, spin–spin and spin–rotation splittings were resolved and analyzed for both electronic states. More recently, Boudjarane et al. used this same technique to analyze the spin splitting parameters in the (1,1) transition of the \( \chi^{2}\Sigma_{u}^{+}-\chi^{2}\Sigma_{g}^{+} \) spectrum.\(^{141}\) Improved constants for the (1,0) band were also obtained. Table 3 displays selected molecular constants obtained by these authors. Finally, Zackrisson et al. used velocity modulation spectroscopy to observe the (0,1) transition of \( \chi^{2}\Sigma_{u}^{+}-\chi^{2}\Sigma_{g}^{+} \).\(^{142}\) These authors analyzed a spin–orbit interaction between the \( \chi^{2}\Sigma_{u}^{+} \) state and the nearby \( 2\Pi \) state.

Recent theoretical studies of \( \text{C}_2^{+} \) include the MRDCl calculations of Bruna et al.\(^{143}\) and the large-scale coupled cluster calculations of Watts and Bartlett.\(^{127}\) These latter authors calculated the equilibrium bond lengths, the vibrational frequency, the dissociation energy, and the electronic term energies for the ground \( \chi^{2}\Sigma_{g}^{+} \) state and three excited electronic states. The \( \text{C}_2^{2+} \) dication has also been studied theoretically.\(^{144}\)

VI. \( \text{C}_3 \)

A. Early Experimental Work

The spectroscopy of \( \text{C}_3 \) has a long and rich history, and only a brief outline will be given here. Wettlaufer and Van Zee provided an excellent discussion of the early developments in their review article.\(^{1}\) The \( \text{A}^{2}\Pi_{u}-\chi^{2}\Sigma_{g}^{+} \) emission spectrum of \( \text{C}_3 \), near 4050 Å, was first observed from the tail of a comet by Huggins in 1882.\(^{145}\) These same bands were later observed in the laboratory by Herzberg in 1942,\(^{146}\) and were finally identified by Douglas in 1951.\(^{4}\) Rotational analysis of the \( \text{A}^{2}\Pi_{u}-\chi^{2}\Sigma_{g}^{+} \) bands was consistent with a linear structure for \( \text{C}_3 \) in both the ground and upper electronic states. However, very early on it was recognized that the ground-state \( \nu_2 \) bending frequency was extraordinarily low, about 63.3 cm\(^{-1}\), indicating extremely anharmonic, large amplitude bending motion.\(^{147}\) The spectroscopic characterization of gas-phase and matrix-isolated \( \text{C}_3 \) continued through the 1980s, resulting in the assignment of most of the ground and upper state vibrational frequencies in the \( \text{A}^{2}\Pi_{u}-\chi^{2}\Sigma_{g}^{+} \) band (except \( \nu_9 \) in the upper state), the characterization of the unusually large Renner–Teller effect in the \( \text{A}^{2}\Pi_{u} \) state, and the discovery and characterization of a low-lying triplet electronic state manifold.\(^{148–152}\) In 1988, several rotational absorption transitions arising from the \( \nu_9 \) fundamental vibration of \( \text{C}_3 \) were discovered in the circumstellar shell of a carbon star by Hinkle et al. (see Figure 6).\(^{2}\) This same year a detailed characterization of the ground-state antisymmetric stretch vibration was accomplished by Hirota and co-workers using rotationally resolved infrared diode laser spectroscopy of \( \text{C}_3 \) clusters produced in a laser photolysis cell.\(^{100,153}\) Many of the transitions observed were hot bands arising from excited bending levels. Analysis of these bands revealed unusual behavior of the \( \text{C}_3 \) bending mode, leading these authors to speculate on the possibility of a quasilinear bending potential. Below, we recount the new developments that have taken place since 1989.

B. Mid-IR and Far-IR Spectroscopy

Schmuttenmaer et al. performed a direct measurement of the low-frequency \( \nu_2 \) bending vibration of \( \text{C}_3 \) using a tunable far-infrared laser spectrometer.\(^{154}\) Rotationally cold clusters (\( T_{rot} \approx 10 \text{ K} \) ) were produced by laser vaporization of graphite in a supersonic molecular beam source. Six \( P-\), \( Q-\), and \( R-\) branch rovibrational transitions were measured with uncertainties in the line positions of about 0.000 02 cm\(^{-1}\). Figure 7 displays the experimentally observed \( Q(6) \) rovibrational transition. This high precision measurement permitted an extremely accurate determination of the ground- and excited-state molecular parameters for the \( \nu_2 \) bending state to be performed. Table 4 presents the ground- and excited-state molecular parameters. Due to the nuclear spin statistical weight of \( ^{12}\text{C}_3 \) (\( I = 0 \)), only rotational levels of positive parity are present. Therefore, the selection rules \( s \leftrightarrow s \) and \( s \leftrightarrow t \) prevent the \( \nu_2 \) frequency from being measured by combination differences of infra-
found the $v_2$ band to be less intense than $v_3$ by only a factor of 2, in much better accord with the experimental observation.\textsuperscript{156}

Szczepanski and Vala measured the $v_1 + v_3$ combination mode of C$_3$ and its isotopomers trapped in solid Ar and Kr using FTIR spectroscopy.\textsuperscript{157} The frequency of the $^{12}$C$_3$ band was 3245 cm$^{-1}$ in Ar and 3243 cm$^{-1}$ in Kr. From a normal-mode analysis of several isotopomers, the authors concluded that C$_3$ was bent in Ar and Kr matrices with a bond angle of 160.0°. This analysis also predicted a $v_2$ frequency for C$_3$ in the matrix of 82 cm$^{-1}$, which agrees with a phosphorescence measurement of 2$v_2 = 175$ cm$^{-1}$ in solid Ne.\textsuperscript{151} but is about 20% larger than the gas-phase value. The large matrix shifts of both the $v_2$ and the $v_3$ frequencies, as well as the negligible shift observed for $v_3$, were also rationalized in terms of a bent structure. The authors found support for a bent geometry observed in these matrices in ab initio calculations by Kraemer et al.\textsuperscript{155} and a MORBID analysis of rovibronic data by Jensen.\textsuperscript{158} However, both of these works have since been superseded by more rigorous experimental and theoretical studies, in which the equilibrium structure is found to be linear, with a flat potential minimum, to be discussed in the next section.\textsuperscript{159,160} Therefore, it seems that the agreement between the matrix structure and these earlier studies is simply fortuitous. The matrix behavior of C$_3$ appears to be similar to that of triplet C$_4$, also discussed below. In that case, all theoretical and experimental evidence support a linear structure.

Table 4. Molecular Parameters of the Fundamental Vibrations in the X$^3Π_{1/2}$ Ground State of C$_3$\textsuperscript{a}

<table>
<thead>
<tr>
<th>parameter</th>
<th>experiment</th>
<th>theory\textsuperscript{a}</th>
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<tbody>
<tr>
<td>(000)</td>
<td>B$_0$ (cm$^{-1}$)</td>
<td>$^{12}$C$_3$</td>
</tr>
<tr>
<td></td>
<td>D$_0$ (10$^{-3}$ cm$^{-1}$)</td>
<td>0.1472(13)\textsuperscript{f}</td>
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<tr>
<td></td>
<td>r$_0$ (Å)</td>
<td>1.2794(7)\textsuperscript{f}</td>
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<tr>
<td>(010)</td>
<td>v$_0$ (cm$^{-1}$)</td>
<td>63.416529(40)\textsuperscript{f}</td>
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<tr>
<td></td>
<td>B (cm$^{-1}$)</td>
<td>0.4424068(52)\textsuperscript{f}</td>
</tr>
<tr>
<td></td>
<td>D (10$^{-3}$ cm$^{-1}$)</td>
<td>0.2361(16)\textsuperscript{f}</td>
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<tr>
<td></td>
<td>q (cm$^{-1}$)</td>
<td>0.0005694(2)\textsuperscript{f}</td>
</tr>
<tr>
<td>(100)</td>
<td>v$_0$ (cm$^{-1}$)</td>
<td>1226.6\textsuperscript{g}</td>
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<tr>
<td></td>
<td>B (cm$^{-1}$)</td>
<td>0.41985(89)\textsuperscript{a}</td>
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<td></td>
<td>D (10$^{-3}$ cm$^{-1}$)</td>
<td>1.552(23)\textsuperscript{f}</td>
</tr>
<tr>
<td>(001)</td>
<td>v$_0$ (cm$^{-1}$)</td>
<td>2040.0192(6)\textsuperscript{f}</td>
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<td>B (cm$^{-1}$)</td>
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<td>D (10$^{-3}$ cm$^{-1}$)</td>
<td>0.4328(31)\textsuperscript{f}</td>
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<tr>
<td>(000)</td>
<td>B$_0$ (cm$^{-1}$)</td>
<td>$^{12}$C$_3$</td>
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<tr>
<td></td>
<td>D$_0$ (10$^{-5}$ cm$^{-1}$)</td>
<td>0.1398(42)\textsuperscript{f}</td>
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<td>(001)</td>
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<td>2027.2078(5)\textsuperscript{f}</td>
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<td>B (cm$^{-1}$)</td>
<td>0.418743(23)\textsuperscript{f}</td>
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<tr>
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<td>D (10$^{-3}$ cm$^{-1}$)</td>
<td>0.1398(42)\textsuperscript{f}</td>
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<tr>
<td>(000)</td>
<td>B$_0$ (cm$^{-1}$)</td>
<td>$^{13}$C$_3$</td>
</tr>
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<td></td>
<td>D$_0$ (10$^{-5}$ cm$^{-1}$)</td>
<td>0.128903(13)\textsuperscript{f}</td>
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<td>r$_0$ (Å)</td>
<td>1.29452</td>
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<tr>
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<td>1961.9488(3)\textsuperscript{f}</td>
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<td>B (cm$^{-1}$)</td>
<td>0.4101376(16)\textsuperscript{f}</td>
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<tr>
<td></td>
<td>D (10$^{-3}$ cm$^{-1}$)</td>
<td>0.3470(45)\textsuperscript{f}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Numbers in parentheses are uncertainties in the last digits.\textsuperscript{b} Theoretical values are from a potential energy surface calculated at the CCSD(T)/177cGTO level using the discrete variable representation.\textsuperscript{80} \textsuperscript{c} Tunable far-infrared laser spectroscopy.\textsuperscript{154} \textsuperscript{d} SEP spectroscopy.\textsuperscript{89} \textsuperscript{e} Infrared diode laser spectroscopy.\textsuperscript{151} \textsuperscript{f} Infrared diode laser spectroscopy.\textsuperscript{163}
for gas-phase C₄, whereas ESR studies of triplet C₄
trapped in Ar and Ne was interpreted in terms of a
slightly bent structure. This interesting matrix
effect deserves further investigation.

Finally, Moazzzen-Ahmadi and Mckellar have re-
ported infrared diode laser observations of the ν₃
fundamental and the (ν₂ + ν₃) – ν₂ hot band of ¹²C₃,
as well as the ν₃ fundamental of ¹³C¹²C¹³C in the gas
phase. Table 4 presents molecular constants ob-
tained for these isotopomers.

C. Electronic Spectroscopy

1. The 'Σ₉' Ground State

The A'Πₐ – X'Σ₉ᵊ band system of C₃ has been stud-
ied extensively for many years. Weltner and Van
Zee described early gas-phase and matrix studies of
this band, which characterized the ground-state
vibrational frequencies for several bending levels and
stretch–bend combination levels. From these stud-
ies, it was recognized that C₃ possesses a very
unusual ground-state potential surface, characterized
by floppily bending motion and strong stretch–bend
coupling interactions. The data seemed to indicate
that the molecule may be quasilinear, with a barrier
to the linear configuration that increases upon exci-
tation of the antisymmetric stretch and decreases as
the symmetric stretch is excited. Jensen used a
MORBID Hamiltonian to analyze the bending po-
tential, whereby parameters of an effective potential
were fitted to experimentally determined vibronic
energy levels. This study yielded a barrier to linearity
of 16.5 cm⁻¹ and an equilibrium bond angle of
165.2°, which was also in agreement with ab initio
calculations performed by Kraemer et al.

Dispersed fluorescence (DF) and stimulated emis-
sion pumping (SEP) measurements of C₃ seeded in
a molecular beam, performed by Rohlfing and Gold-
smith and Northrup and Sears, have greatly
increased the number of measured ground-state vibronic
levels. Rohlfing and Goldsmith measured
a large number of vibronic transitions using the DF
technique after excitation to the A'Πₐ state and a
higher-lying UV state. Assignment of the DF spectra
yielded frequency positions and molecular constants
for ground state (ν₁, ν₂, ν₃) energy levels up to 17 000
cm⁻¹. These included states for which the vibra-
tional quantum numbers were in the range 0 ≤ ν₁ ≤ 8,
0 ≤ ν₂ ≤ 37, and 0 ≤ ν₃ ≤ 4. SEP studies were then used
to measure high resolution (0.08 cm⁻¹) spectra of the
(0ν₃) (ν₂ = 1–13) and (6ν₂) (ν₂ = 1–5) states in the
ground state of the UV band system. Similar mea-
surements were performed on the (0ν₂) (ν₂ = 0–8)
and (0ν₄) (ν₂ = 0–14) antisymmetric stretch–bend
combination levels in the ground state of the A'Πₐ –
X'Σ₉ᵊ system. In a parallel study, Northrup and
Sears measured SEP spectra of the pure bending
levels (0ν₃ν₂) (ν₂ = 0–34) and the symmetric stretch–
bend combination levels (1ν₂) (ν₂ = 0–8) and (3ν₂)
(ν₂ = 4–8).

This new DF and SEP data sampled regions of the
potential energy surface that were much higher in
energy than the data set that had been available
previously. Therefore, a more accurate fit of the

Figure 8. (a) Effective bending potentials from a semirigid
bender analysis for X'Σ₉ᵊC₃ plotted vs ρ, the suplemental
bond angle. The solid line is the zero point bending
potential (ν₁ = 0, ν₂ = 0). The dotted curves are due to
excitation of the ν₁ symmetric stretch: (- - -) ν₁ = 1; (- - -)
ν₁ = 2; (- - -) ν₁ = 3; (- - -) ν₁ = 4. (b) Effective bending
potentials due to increasing the ν₃ antisymmetric stretch.
The solid curve is the zero point bending potential and the
dotted curves are for ν₃ = 1–4. The curve styles for each
ν₃ level are the same as above. (Produced from data in ref
39.)
ground-state potential was possible. Northrup et al.
used this extensive data set, along with the infrared
and far-infrared results to fit an effective bending
potential using the semirigid bender analysis. The
results of this analysis revealed that C₃ is not quasilinear
in its ground state as had previously been thought, but rather possesses an extremely flat,
broad potential minimum. A barrier to linearity
appears when the antisymmetric stretch is excited,
which increases upon further excitation. Excita-
tion of the symmetric stretch, on the other hand, results in a more rigid linear configuration.

Several recent ab initio studies have been per-
formed over the past few years that address the
nature of this rather remarkable ground-state po-
tential. The CISD study of Kraemer et al., which
revealed a quasilinear bending potential for C₃, was
superseded by the work of Jørgensen et al. These
authors performed a CASSCF calculation of the
ground-state potential energy surface and the dipole
moment surface. Later, Jensen et al. repeated this
calculation using the full-valence CASSCF. The
qualitative features of the potential energy surface
obtained were in agreement with the semirigid
bender analysis, in that the equilibrium structure
was found to be linear with a flat, broad potential minimum. Also, the calculations correctly predicted the emergence of a barrier to linearity upon $\nu_3$ excitation and the increased harmonicity of the potential with excitation of $\nu_2$.

More recently, Mladenovic et al. investigated the C$_3$ equilibrium geometry, potential energy surface, and rovibrational energies using the CCSD(T) method with large basis sets of contracted Gaussian-type orbitals (cGTO). The highest level of theory employed was CCSD(T)/255 cGTO, which was used to calculate the equilibrium geometry, yielding an equilibrium C=C bond length of 1.294 52(30) Å. An effective zero-point bending potential was obtained using a 222 cGTO basis set that corroborated the experimental potential. Finally, an analytical ground-state potential energy function for all three normal modes was calculated by fitting 108 energy points calculated at the CCSD(T)/177 cGTO level. This potential energy function was then used to calculate the term energies for energy levels up to 3000 cm$^{-1}$. Much more quantitative agreement with experiment was achieved with the CCSD(T) method, as compared to the CASSCF calculations, and the strong stretch was achieved with the CCSD(T) method, as compared to the CASSCF calculations, and the strong stretch

Table 4 compares these theoretical calculations with the experimental parameters for the ground-state fundamental vibrations. A complete set of experimental parameters can be found in ref 40.

2. The A$^1\Pi_u$ State

In addition to the unusual dynamics present in the ground state of the A$^1\Pi_u$–X$^1\Sigma_g^+$ band, the excited state was also found to exhibit its own unique properties. Many of the low-lying energy levels of the A$^1\Pi_u$ state were assigned in the 1965 work of Gausset et al. Subsequently, numerous gas-phase and matrix experiments have been performed to characterize the band system. According to Weltner and Van Zee, the vibrational frequencies of the symmetric stretch and the bending modes in the A$^1\Pi_u$ state were measured as $\nu_1 = 1085.8$ cm$^{-1}$ and $\nu_2 = 307.9$ cm$^{-1}$. Such a large increase in the excited electronic state bending frequency was thought to be due to the occupation of the $\pi_0$ antibonding orbital, which stabilizes the linear configuration. The interaction of the bending vibration with the excited electronic configuration produces a strong Renner–Teller effect that splits the degeneracy of the electronic state into positive and negative symmetry components. This effect is particularly intriguing in C$_3$ due to the large amplitude of the bending mode. Thus, the A$^1\Pi_u$ state has become a prototype system for studying Renner–Teller interactions in linear polyatomic molecules.

While most of the recent effort to study the A$^1\Pi_u$–X$^1\Sigma_g^+$ band system has focused on the ground state, significant progress on the upper state has also been made. At the time of Weltner and Van Zee's review, no definitive assignment of the $\nu_3'$ frequency had been made. The nature of the antisymmetric stretch vibration in the A$^1\Pi_u$ state has been the source of some controversy over the intervening years and has only been resolved recently. Earlier estimates placed this frequency somewhere between 650 and 900 cm$^{-1}$. Recent attempts to measure $\nu_3'$ included the work of Balfour et al., whose tentative assignment of $2\nu_3'$ suggested a frequency of 808 cm$^{-1}$. Also, Baker et al. proposed an assignment of the (001)–(001) transition, leading to an estimate of 890.2 cm$^{-1}$ for $\nu_3'$. All of these estimates place $\nu_3'$ substantially lower than the $\nu_3''$ frequency in the ground state, indicating a large increase in the anharmonicity of the antisymmetric stretch in the A$^1\Pi_u$ state. However, a consensus on the exact value of the upper state frequency was reached only after the recent work of Izuha and Yamanouchi. These authors observed new vibronic bands in the A$^1\Pi_u$–X$^1\Sigma_g^+$ system by laser induced fluorescence of C$_3$ clusters produced in a laser vaporization–supersonic expansion source. In particular, a series of vibronic bands in the 389–337 nm region were found to exhibit rotational structure characteristic of $^1\Sigma_u^+-^1\Sigma_g^+$ symmetry. $^1\Sigma_u^+$ vibronic symmetry in the A$^1\Pi_u$ state can occur through the Herzberg–Teller interaction with a higher-lying $^1\Sigma_u^+$ state and is realized only when both the $\nu_2''$ and the $\nu_3'$ quantum numbers take odd values. (The $\nu_3'$ states are labeled with + or − signs according to the symmetry of the Renner–Teller state.) Therefore, the lowest energy vibronic band in this region was assigned as the (01$^+$1)–(000) transition in the A$^1\Pi_u$–X$^1\Sigma_g^+$ system. Given the known frequency of the (01$^+$1)–(000) transition, it was then possible to estimate $\nu_3$ to be about 539 cm$^{-1}$. This result was in conflict with the study by Baker et al., who assigned hot band transitions arising from the (001) ground state. One of these hot bands was tentatively assigned as the (001)–(000) transition, leading to the estimate of 890.2 cm$^{-1}$ for $\nu_3'$ as mentioned above. Izuha and Yamanouchi's measurement implied a (001)–(001) transition frequency of 23 174 cm$^{-1}$, which is lower than the band assigned by Baker et al by 352 cm$^{-1}$. A direct measurement of the (001)–(001) transition by Izuha and Yamanouchi revealed a transition frequency of 23 177.174 cm$^{-1}$, leading to a $\nu_3'$ frequency of 541.7 cm$^{-1}$. Furthermore, these authors reassigned the band observed by Baker et al. to the (02$^+$1)–(001) transition. Izuha and Yamanouchi's work placed the $\nu_3'$ frequency lower than any previous estimate and implied an even larger anharmonicity along the antisymmetric stretch coordinate in the A$^1\Pi_u$ state than previously thought. Selected molecular parameters for the A$^1\Pi_u$ state are given in Table 5. A complete list of all the observed transitions in the A$^1\Pi_u$ state can be found in refs 98 and 166.

3. The $^1\Sigma_u^+$ State

$^1\Sigma_u^+$ is the next excited state above A$^1\Pi_u$ in the singlet manifold. Although the oscillator strength of the $^1\Sigma_u^+-X^1\Sigma_g^+$ band system is predicted to be very large ($f \sim 0.92$), it has been notoriously difficult to observe. Extrapolation of the $^1\Sigma_u^+-X^1\Sigma_g^+$ band origins that have been measured for C$_7$ through C$_{15}$ down to C$_3$ leads to a value of 170 nm for this band. Chang and Graham tentatively assigned a series of
Table 5. Molecular Parameters of C3 in the A^3Π_u, a^3Π_u, and b^3Π_g States

| Parameter | Experiment | Theory
<table>
<thead>
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<tbody>
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<td>A^3Π_u (000)</td>
<td>T (cm^-1)</td>
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<td>( f_0 ) (Å)</td>
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<td></td>
<td>( \lambda_0 ) (cm^-1)</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>( \gamma_0 ) (cm^-1)</td>
<td>259</td>
</tr>
<tr>
<td></td>
<td>( \alpha_0 ) (Å)</td>
<td>1.2980</td>
</tr>
<tr>
<td>b^3Π_g (000)</td>
<td>T (cm^-1)</td>
<td>16930</td>
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<tr>
<td></td>
<td>( A_0 ) (cm^-1)</td>
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<tr>
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<td>( B_0 ) (cm^-1)</td>
<td>0.4169(047)</td>
</tr>
<tr>
<td></td>
<td>( D_0 ) (10^-15 cm^-5)</td>
<td>0.030(5)</td>
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<td></td>
<td>( \lambda_0 ) (cm^-1)</td>
<td>0.053(5)</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>( \alpha_0 ) (Å)</td>
<td>1.2863(1)</td>
</tr>
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Numbers in parentheses are uncertainties in the last digits. From a theory of the Renner–Teller effect. 169 LIF spectroscopy. 166 Distributed feedback diode laser spectroscopy. 171

absorption transitions observed in an Ar matrix near 189 nm to the \( ^1Σ_u^-PX^1Σ_g^+ \) band of C3, although this assignment has not been confirmed. 168 Part of the reason for the difficulties in observing this band may be due to strong interactions of the \( ^1Σ_u^- \) state with other excited electronic states, including A^3Π_u, as discussed above, as well as states in the triplet manifold. These interactions may distribute the intensity of the band over a very large energy range.

4. The a^3Π_u and b^3Π_g States

The metastable a^3Π_u state was first observed through the a^3Π_u–X^1Σ_g^+ phosphorescence transition in Ar and Ne matrices. 148 The mechanism for populating the a^3Π_u state was intersystem crossing from the (000) level of the A^3Π_u state. Recently, Sasada et al. 169 detected the b^3Π_g–a^3Π_u band system in the gas phase by measuring absorption from the a^3Π_u state using a distributed-feedback diode laser spectrometer with a precision of about 0.001 cm^-1. Emission from the b^3Π_g state was also observed with a Fourier transform spectrometer. C3 molecules were prepared in the excited triplet states in a hollow cathode acetylene discharge. The lifetime of the a^3Π_u state in the discharge cell was estimated to be about 50 µs as compared to a lifetime of 20 µs observed in the neon matrix. The rovibrionic spectrum, centered at 6482.4 cm^-1, displayed splitting patterns characteristic of a triplet electronic state and also showed evidence for perturbation of the b state. Analysis of the band yielded the molecular constants for both the a and b states, some of which are shown in Table 5. Although a definitive vibrational assignment could not be made for this band, there was no evidence for bending excitation in either state, due to the absence of Renner–Teller splittings.

Smith et al. performed a more recent FTIR study of the a^3Π_u state in order to assign some of the vibrational structure both within the a state and in transition to the b state. 170 In these experiments, the a^3Π_u state was populated by laser excitation of C3 trapped in solid Ar or Ne to the A^3Π_u state, followed by intersystem crossing. Direct FTIR absorption spectra were then recorded from the a state. Several vibrational transitions within the a state were observed, including a band at 1455.3 cm^-1, which was assigned as \( v_3 \), and a band at 2609 cm^-1, assigned as \( v_1 + v_3 \). Further evidence was provided for assignments using isotopic substitution. b^3Π_g–a^3Π_u vibronic transitions were observed as well. In particular, the matrix studies confirmed that the band measured in the gas phase by Sasada et al. 169 was the vibrationless origin. Tentative assignment of a band in the b state at 1303 cm^-1 to the \( v_1 \) stretch was also made. The assignment by Smith et al. of the \( v_3 \) mode in the a^3Π_u state was recently confirmed by the gas-phase measurements of Hwang et al. 171

These authors used infrared diode laser spectroscopy of a^3Π_u C3 produced in a hollow cathode discharge to observed the rotationally resolved \( v_3 \) absorption spectrum centered at 1449.5255(22) cm^-1. Rotational and centrifugal distortion constants, spin–spin and spin–rotation interaction constants, A-doubling parameters, and spin–orbit coupling constants were all determined from the rotational analysis. Molecular parameters for C3 in the vibrationless levels of the a^3Π_u and b^3Π_g can be found in Table 5.

Recently, Tokaryk and Civis observed b^3Π_g–a^3Π_u gas-phase emission spectra that involved transitions between excited bending vibrational energy levels in both the ground and upper states. 172 C3 was prepared in the excited states using a methane discharge, and a Fourier transform spectrometer with a precision of 0.005 cm^-1 was used to record the spectra. Both 12C3 and 13C3 bands were observed. These experiments afforded the authors a rare opportunity to study the Renner–Teller effect in a triplet electronic state, which was found to be large in both states. The following bands and their vibronic symmetries were analyzed in this work: (010)\(^2Σ_u^+\)–(001)\(^2Σ_g^+\), (010)\(^2Σ_u^-\)–(001)\(^2Σ_g^-\), (010)\(^2Δ_u\)–(010)\(^2Δ_g\), (020)\(^4Φ_g\)–(020)\(^4Φ_u\), and (030)\(^2Γ_g\)–(030)\(^2Γ_u\). Since these were all sequence bands, the Renner–Teller splittings and the bending vibrational energies for the two states could not be measured directly. However, an analysis of the spin–orbit parameters for the transitions yielded the value for the upper state Renner parameter \( \epsilon \) of +0.447 and \( \epsilon' = -0.566 \) for the lower state. These large, positive values for the Renner parameters are an indication of significant coupling between the bending vibrational and electronic angular momenta. From the Renner parameters, it was possible to estimate \( v_3 \) for the upper and lower state. For the \( a \) state \( v_3 \) was found to be \( \sim 505 \) cm^-1, and for the \( b \) state \( v_3^b \) was \( \sim 345 \) cm^-1. Again, the analysis of the \( b \) state was complicated

...
by perturbations, the nature of which are as yet undetermined.

5. Other Band Systems

Lemire et al. observed a UV band system in the 266–302 nm region using resonant two photon ionization spectroscopy of C₃ produced in a pulsed supersonic expansion by laser ablation. Dispersed fluorescence and SEP measurements due to excitation to this upper electronic state were discussed earlier in the description of Rohlfing and Goldsmith's work. The vibronic symmetry of the band system was found to be \(^3\Sigma^+_u - \Sigma^+_g\) with the bands arising from the (000) level of the ground electronic state. Lifetimes of the upper state vibronic levels ranged from 0.4 to 2.5 \(\mu\)s, which is consistent with a spin allowed transition. However, the low oscillator strength that was observed (f \(\sim 0.001\)) indicated that the transition was electric dipole forbidden. Thus, the authors proposed that the upper state was either \(^1\Pi_g\) or \(^1\Delta_g\) or possibly both. Oscillator strength for this band system was thought to result from mixing with the nearby \(^1\Sigma^+_u\) state through the Herzberg–Teller interaction.

D. C₃ in the Interstellar Medium

Emission due to the A\(^1\Pi_g - X^1\Sigma^+_g\) band of C₃ was first detected in the tail of a comet as early as 1882, and its \(v_3\) infrared absorption spectrum was observed more recently in the circumstellar shell of a carbon star as mentioned above. Recent efforts have been devoted to detecting the molecule in cold interstellar molecular clouds. Since numerous carbon chain molecules have been detected in these sources, it has been speculated that pure carbon clusters are present as well. However, since C₃ is nonpolar, the standard millimeter wave astronomy methods cannot be used to detect these clusters. Rather, we have sought to exploit the low-frequency bending vibration to perform far-infrared astronomy measurements. Precise laboratory far-infrared measurements of the \(v_2\) bending mode of C₃ were used to design a far-infrared astronomy search using a heterodyne detector on board the Kuiper Airborn Observatory. Figure 9 displays the spectrum that was observed toward the Sagittarius B2 star forming region. The weak absorption signal at 63.7 km s\(^{-1}\) relative to the local standard of rest (LSR) has been tentatively identified as the R(2) transition of the C₃ bending mode. An LSR velocity near 63 km s\(^{-1}\) is characteristic of molecules near the core of Sgr B2.

Haffner and Meyer studied optical emission spectra from a translucent molecular cloud toward the star HD 147889. They observed a weak emission feature at 4051.6 Å, which was tentatively assigned as blended Q-branch transitions of the A\(^1\Pi_g - X^1\Sigma^+_g\) spectrum of C₃. P- and R-branch lines were not observed due to spectral congestion. From these two studies, it appears that C₃ is indeed present in the cold interstellar medium, although it is clearly difficult to detect. Unless larger carbon clusters are more abundant than C₃ in these sources, improvements in the signal-to-noise ratio may be necessary before detection of the larger species becomes feasible.

E. C₃⁻

Theoretical calculations predict that C₃⁻ is linear with a \(^2\Pi_g\) ground electronic state. Raghavachari calculated structures, atomization energies, and vibrational frequencies at the QCISD(T)/6-31G* level. In particular, he predicted that the \(v_2\) bending vibration should occur at 399 cm\(^{-1}\), which is substantially larger than the bending frequency for neutral C₃. This is indicative of a much more harmonic bending frequency for the anion due to the added stability imparted to the linear configuration by an additional electron in the \(\pi\) shell. More recently, Schmatz and Botschwina carried out large-scale coupled cluster calculations to study the linear ground state of C₃⁻. These authors determined the equilibrium bond length to be 1.307 Å and the \(v_3\) symmetric stretch frequency to be 1177 cm\(^{-1}\) at the RCCSD(T)/255 cGTO level.

Until very recently, the only experimental technique used to measure ground-state vibrational frequencies of carbon cluster anions was the analysis of hot band transitions in anion photoelectron spectroscopy. Arnold et al. used this technique to measure a \(v_1\) symmetric stretch frequency of 1075 ± 100 cm\(^{-1}\) for C₃⁻. In good agreement with the RCCSD(T) prediction. Szczepanski et al. have recently reported direct infrared absorption spectroscopy measurements of linear carbon cluster anions trapped in Ar matrices. The clusters were formed by depositing laser vaporized graphite in the matrix and then irradiating with an electron beam or an Ar plasma to form anions. Figure 10 displays a region of the infrared spectrum obtained in this way. The authors assigned an absorption band at 1721.8 cm\(^{-1}\) to the \(v_3\) antisymmetric stretch. Measurements of
calculated at the CCSD(T)/[4s3p2d1f] level of theory.184 A bond length of 1.324 Å and a bond angle of 67.8° was found for the linear isomer, the calculated bond lengths were 1.284 and 1.306 Å for the inner and outer bond lengths, respectively, at this level. The authors attempted to characterize the effect of the basis set on the relative isomer energies by performing the calculations over all possible 13C-substituted isotopomers confirmed this assignment,178 which is also in agreement with Raghavachari’s prediction of 1754 cm⁻¹ for this band.174

VII. C₄

A. Theory

Ab initio calculations predict that the even-numbered carbon clusters C₄, C₆, and C₈ possess two low-energy structural isomers, a linear chain with a 3B₂ electronic state, and a 1B₁g cyclic ring. An enormous number of theoretical studies have appeared in the literature on the C₄ cluster. These calculations have addressed the geometric structural parameters of various isomers, relative stabilities, vibrational frequencies and intensities, electronic structure, and thermodynamic properties. Most theoretical predictions agree on the two lowest energy structures, the cumulenic linear chain, and a bicyclic rhombic structure. (See Figure 1.) However, there has been considerable disagreement over which of these structures is the true global minimum. Theoretical calculations that have appeared since the Weltner and Van Zee review include a configuration interaction study of the electronic structure of linear C₄, C₆, C₈, and C₁₀ by Liang and Schaefer.186 In addition, Andreoni et al. used the Car–Parrinello method to obtain optimized structures for C₄ and C₆.187 Adamowicz used first-order correlation orbitals to calculate electron affinities for both isomers of C₄ at the coupled cluster level.95 Lammertsma et al. investigated the unusual nature of the cross-ring bond of the rhombic isomer using MP4 calculations.188 Nygren and Pettersson used an internally contracted averaged coupled pair functional method to predict the lowest dipole allowed electronic transition of rhombic C₄,189 finding a B₁u→A₁g transitions to occur at about 16,000 cm⁻¹.

Martin et al. studied the geometries, energetics, and vibrational frequencies of C₄ ab initio.190 The geometry and frequency calculations were performed at the MP2 level, and the relative energies were obtained at the QCISD(T) level. They found the linear–cyclic energy difference to be 4.23 kcal/mol in favor of the rhombic structure. On the basis of their harmonic frequency calculations, these authors tentatively assigned a matrix absorption at 1284 cm⁻¹ to cyclic C₄. Parasuk and Almlof studied geometric and electronic structures and relative energies of the cumulenic and polyacetylenic linear chains and the rhombic structure at the CASSCF and MRCl levels.70 These authors found the cumulenic linear structure to be slightly lower in energy than the rhombus. However, the relative energies were strongly influenced by the size of the basis set used, and larger basis sets tended to lower the energy of the rhombic structure. The linear acetylenic structure was found to occur at higher energies. They also investigated the possibility that linear C₄ may be slightly bent, as suggested by ESR studies,161,162 by calculating a potential function for bending. They found the potential function to be very harmonic, indicating that triplet C₄ is linear and relatively (with respect to C₃) rigid.

The largest scale calculations that have been performed on C₄ to date are those of Watts et al. at the CCSD(T) level of theory.71 These authors employed large basis sets, which included f and g functions, to calculate structures, vibrational frequencies, and relative energies for the ground electronic states of the cumulenic chain and the bicyclic ring. Geometries, frequencies, and IR intensities were obtained using various basis sets, the largest and most complete being the PVTZ basis. For the linear isomer, the calculated bond lengths were 1.284 and 1.306 Å for the inner and outer bond lengths, respectively, at this level. The authors attempted to characterize the effect of the basis set on the relative isomer energies by performing the calculations over...
a range of basis sets. They found the relative energies to be extremely sensitive to the size of the basis and the type of basis employed, although the effect of increasing the polarization of the basis functions, as well as inclusion of triple excitations, tended to favor the rhombus. The highest level calculations performed (CCSD(T)/PVTZ) revealed the rhombic isomer to be the lowest energy structure, but only by about 1 kcal/mol.

Martin and Taylor recently studied the isomers of C\textsubscript{2}–C\textsubscript{10} at the CCSD(T) level using correlation consistent basis sets.\textsuperscript{38} The aim of this study was to examine, in detail, the vibrational spectra and to attempt assignments of some of the unknown transitions in the spectrum of carbon clusters trapped in matrices. More recently, Martin et al. reevaluated their earlier assignment of the 1284 cm\textsuperscript{-1} matrix band to the \nu\textsubscript{6} band of cyclic C\textsubscript{4}.\textsuperscript{191} The authors constructed a quartic force field at the CCSD(T) level and found a strong Fermi resonance interaction between the \nu\textsubscript{6} mode and the \nu\textsubscript{3} + \nu\textsubscript{5} combination mode. This interaction raised the perturbed band origin to 1320 ± 10 cm\textsuperscript{-1}, casting doubt on the earlier assignment.\textsuperscript{190}

Given the remarkable sensitivity of the linear–cyclic energies, as well as the spectroscopic parameters, to the details of the calculation, it is quite apparent that experimental constants are badly needed for the cyclic system.

B. Experiment

1. The Rhombic Isomer

The goal of characterizing the rhombic isomer of C\textsubscript{4} by direct high-resolution spectroscopic measurements continues to elude researchers. Evidence for a rhombic C\textsubscript{4} isomer has been obtained by researchers using Coulomb explosion imaging.\textsuperscript{192,193} In this technique, carbon cluster anions are produced by Cs ion sputtering of a graphite surface. The ions are then mass selected and accelerated to 12 MeV, and the electrons are photodetached by a UV laser intersecting the beam. The neutral clusters are then atomized in an “explosion” that results from electron stripping in a high-field region. From the spatial distribution of the charged fragments, it is possible to infer the structure of the molecule before the explosion occurred. Algranati et al. observed the rhombic C\textsubscript{4} cluster using this technique.\textsuperscript{192} Later, Kella et al. used a combination of Coulomb explosion imaging and laser photodetachment to characterize the isomers of C\textsubscript{4}.\textsuperscript{193} The observation of three distinct photodetachment wavelengths was taken as evidence for three different structural isomers for the anions and the neutrals. Coulomb explosion after photodetachment at each wavelength revealed the three structures to be linear, rhombic, and three-dimensional. The three-dimensional structure was assumed to be tetrahedral, although no other experimental or theoretical evidence exists for this isomer. A weakness in the Coulomb explosion approach is the lack of knowledge of the vibrational state distribution of the neutral fragment prior to the explosion.

Vibrational excitation in these floppy systems could obscure the analysis of the fragmentation pattern.\textsuperscript{180}

2. The Linear Isomer

Much progress has been made toward the characterization of linear C\textsubscript{4} since the publication of Weltner and Van Zee’s review. Linear C\textsubscript{4} was first observed using electron spin resonance (ESR) spectroscopy of carbon clusters trapped in solid Ne and Ar matrices by Graham et al.\textsuperscript{194} The results were consistent with a linear \Sigma\textsuperscript{3} structure. Later, Cheung and Graham observed ESR spectra of C\textsubscript{4} trapped in an Ar matrix, in which the clusters were produced by UV photolysis of C\textsubscript{6}H\textsubscript{3}.\textsuperscript{161} Under these conditions, the ESR line widths were more than 10 times narrower than had been observed in the previous experiments, revealing splittings to the \nu\textsubscript{3} and \nu\textsubscript{5} lines that were interpreted as evidence for a slightly bent structure. The authors ruled out the possibility that the splitting could arise from nonequivalent matrix sites since no changes in the splittings were observed after annealing the matrix. Jiang and Graham later repeated the ESR measurements for C\textsubscript{4} trapped in a Ne matrix.\textsuperscript{162} Since the same splittings were observed in Ne as in Ar, the authors reasoned that, if the observed splittings were caused by interactions with the matrix, then these interactions should change for the different matrices. Otherwise, the bent structure might be an intrinsic property of the molecule. However, no evidence for a bent structure of gas-phase C\textsubscript{4} has been obtained, either from ab initio theory, as discussed above, or from subsequent gas-phase measurements. Additional support for a bent structure in matrices was initially claimed by Shen et al. from the assignment of an IR absorption band at 1699.8 cm\textsuperscript{-1} to \nu\textsubscript{5} + \nu\textsubscript{5} stretch–bend combination band of cis-bent C\textsubscript{4} in an Ar matrix.\textsuperscript{195} However, this band was recently reassigned to \nu\textsubscript{5} antisymmetric stretch of the C\textsubscript{4}–carbon cluster anion.\textsuperscript{196}

Prior to the Weltner and Van Zee review, numerous infrared absorption transitions had been observed from polyatomic carbon clusters trapped in cryogenic matrices, but there was great confusion as to the assignments of these bands. For example, Thompson et al. tentatively assigned a matrix absorption at 1544 cm\textsuperscript{-1} to linear C\textsubscript{3} and a band at 2164 cm\textsuperscript{-1} to linear C\textsubscript{4}.\textsuperscript{197} Subsequent ab initio calculations suggested a much lower frequency for C\textsubscript{4} and recommended that these assignments be reversed.\textsuperscript{198} Later, the 2164 cm\textsuperscript{-1} band was reassigned to C\textsubscript{3}, based on isotopic substitution measurements by Vala et al.,\textsuperscript{199} while Shen and Graham confirmed the assignment of the 1544 cm\textsuperscript{-1} band to the \nu\textsubscript{2} antisymmetric stretch of linear C\textsubscript{4}.\textsuperscript{200} More recently, Withen et al. performed Fourier transform far-infrared spectroscopy of C\textsubscript{3} in an Ar matrix in an attempt to observe the \nu\textsubscript{2} bending frequency.\textsuperscript{201} An absorption band at 172.4 cm\textsuperscript{-1} was observed that could be assigned to the C\textsubscript{2} bending mode based on isotopic substitution. Besides the \nu\textsubscript{2} band of C\textsubscript{3} discussed above,\textsuperscript{164} this measurement represents the only bending mode of a linear carbon cluster to be observed directly in the infrared.

Linear C\textsubscript{4} was first detected and characterized in the gas phase by Heath and Saykally, who measured
the $\nu_3$ antisymmetric stretch using tunable infrared diode laser spectroscopy.\textsuperscript{202} The clusters were produced by pulsed UV laser vaporization of graphite and expanded into an Ar jet. Fourteen rovibrational transitions were assigned to the $\nu_3$ fundamental. The observed band origin of 1549 cm$^{-1}$ confirmed the assignment of the matrix band, which was slightly red-shifted from the gas-phase value due to the matrix perturbation effect. Triplet splitting was observed only in the transition arising from the lowest rotational level, but the spin splitting was not analyzed due to the low signal-to-noise ratio for this transition. Moazzen-Ahmadi et al. performed diode laser spectroscopy measurements on this same band by producing the clusters in a hollow cathode acetylene discharge, wherein the observed rovibrational transitions were extended out to N = 35 in both the P- and the R-branch.\textsuperscript{203} These authors found that the rotational assignment of Heath and Saykally was slightly in error and presented a corrected assignment. From the revised rotational constant, a value of 1.30055(5) Å was obtained for the average ground-state C=C bond length, in excellent agreement with the averaged CCSD(T)/PVTZ result of 1.2999 Å.\textsuperscript{71} The average bond length obtained from experiment confirms that linear C$_4$ exists in a cumulenic bonding configuration. Bond lengths for the acetylenic structure were calculated at the CISD/DZP level to be 1.213 and 1.374 Å for the triple and single bonds, respectively, yielding an average bond length of 1.267 Å, which is significantly smaller than the experimental value.\textsuperscript{190} At this same level of theory, the average bond length for the cumulene was 1.300 Å, again in agreement with experiment.

In addition to the fundamental band, Moazzen-Ahmadi et al. also observed ($\nu_3$ + $\nu_3$) – $\nu_3$ hot band transitions.\textsuperscript{203} On the basis of their measurement of $\varphi_b$, the l-type doubling constant for the $\nu_3$ bending mode, it was possible to estimate the lowest bending frequency. This estimated value was 160 ± 4 cm$^{-1}$ in reasonable agreement with the matrix work of Withey et al.\textsuperscript{201} Because of the high temperature of the discharge, the lower rotational lines, for which triplet splittings might be observable, were not measured. Therefore, the spin–spin and spin–rotation interactions have not yet been characterized in the gas phase. Recently, the ($\nu_3$ + $\nu_3$) – $\nu_3$ hot band was also observed by Moazzen-Ahmadi and Thong.\textsuperscript{37} From these measurements, the frequency of the $\nu_3$ bending mode was estimated to be 352 ± 15 cm$^{-1}$. Representative experimental data are displayed in Figure 11. Molecular constants for the fundamental vibrations of C$_4$ are presented in Table 6. All of the gas-phase spectra that have been observed are consistent with that of a relatively rigid linear molecule. The very large amplitude bending motion that was present for C$_3$ is not evident for C$_4$, and there is no evidence for a bent structure in the gas phase. We are left to conclude that the bent structure observed in Ne and Ar matrices is due to some unusual matrix interaction that is apparently present in both matrices.

Additional spectroscopic information for gas-phase linear C$_4$ was provided by the anion photoelectron spectroscopy measurements of Arnold et al.\textsuperscript{41} Carbon cluster anions produced by laser vaporization of graphite were mass selected using time-of-flight techniques. The electrons were then photodetached from the negative ions, and their kinetic energies were measured. Peaks in the electron kinetic energy distribution corresponded to transitions between vibronic states of the anions and the neutrals. Figure 12 displays the photoelectron spectra observed for the even-numbered C$_4$–C$_8$ cluster anions. From these data it was possible to measure vibrational frequencies of the neutral species. In some cases, tentative
assignments of excited electronic states for the anions and the neutrals were made as well. Photoelectron spectroscopy measurements are complimentary to infrared absorption experiments in that only symmetric vibrational states are observed for the linear carbon clusters, as opposed to direct absorption, which only measures antisymmetric vibrations. The photoelectron spectra observed for \( \text{C}_4 \) were consistent with linear structures for both the anion and the neutral. Vibrational frequencies for neutral \( \text{C}_4 \) that were deduced from the spectra were 2032 \( \pm \) 50 cm\(^{-1} \) for the \( \nu_1 \) symmetric stretch and 339 \( \pm \) 55 cm\(^{-1} \) for the \( \nu_4 \) bending mode. This latter result was consistent with the estimate for \( \nu_4 \) deduced from Moazzen-Ahmadi and Thong's hot band analysis.\(^{37} \)

C. Excited Electronic States

Three excited electronic states can be derived from the ground electron configuration of linear \( \text{C}_8 \), the ground \( ^3\Sigma_g^- \) state, a \( \text{^1}\Lambda_g \), and a \( ^1\Sigma_g^+ \) state. Theoretical predictions for the excitation energies of these states as well as two low-lying \( ^3\Pi \) states can be found in Weltner and Van Zee's review.\(^1 \) More recently, Liang and Schaefer calculated the energies of the \( ^3\Sigma_g^- \) ground states, the two symmetry components of the \( \text{^1}\Lambda_g \), and a state that results from mixing of the \( \text{^1}\Lambda_g \) and the \( ^1\Sigma_g^+ \) states, denoted as \( ^1\Sigma_D \) for the even-numbered linear \( \text{C}_4 - \text{C}_{10} \) clusters.\(^{186} \) These calculations were performed at the SCF and CISD levels of theory using the DZP basis. Theoretical predictions for the low-lying electronic states of the rhombic isomer were also given by Weltner and Van Zee. The only calculation on the electronic states of the rhombic isomer to appear since their review is that of Nygren and Petterson mentioned above.\(^{189} \)

Several low-lying excited electronic states of \( \text{C}_4 \) were recently assigned by Neumark and co-workers using photoelectron spectroscopy of mass-selected \( \text{C}_4^- \), produced in a pulsed electric discharge/supersonic molecular beam source.\(^{42} \) These were the \( \text{^1}\Lambda_g, ^3\Sigma_g^-, ^3\Pi_{1g}, ^3\Pi_{2g}, ^1\Pi_{1g}, \) and \( ^1\Pi_{2g} \) states, with term energies of 0.332, 0.93, 0.82, 0.93, 1.16, and 1.41 \((\pm 0.02) \) eV, respectively.

Numerous optical and UV transitions have been observed for carbon clusters trapped in rare gas matrices, which are due to clusters larger than \( \text{C}_3. \)\(^{204,205} \) Assignments for most of these transitions are very tentative. The most conclusive experimental data on the electronic spectra of linear carbon clusters trapped in matrices has been provided since 1995 by Maier and co-workers.\(^{167,206-208} \) These authors used mass selection of carbon cluster anions, produced either in a hot cathode discharge or a Cs ion sputter source. The mass-selected ions were then deposited in a solid Ne matrix. UV/visible and IR absorption spectra of both anionic and neutral carbon clusters in the matrix were then recorded. Neutral carbon clusters were produced from the anions by irradiating the matrix with the output of a medium-pressure Hg lamp. For example, researchers from this group have measured \( ^3\Sigma_g^- - ^3\Sigma_g^+ \) vibronic transitions for even-numbered linear carbon clusters in the \( \text{C}_4 - \text{C}_{10} \) size range.\(^{206-208} \) Figure 13 displays the observed spectra. A near linear dependence of the band origin wavelength on the cluster size has been observed, as would be predicted by the free electron molecular orbital model. The \( \text{C}_4 \) origin was observed at 26 323 \( \pm \) 15 cm\(^{-1} \), which contradicts an earlier assignment of a 22 600 cm\(^{-1} \) band discussed in Weltner and Van Zee's review.\(^1 \) At the same time, the authors also observed the 1547.2 cm\(^{-1} \) vibrational transition.\(^{208} \)
The C4− cluster ion is predicted to be linear with a $^2\Sigma_g^+$ ground electronic state. Using coupled cluster techniques, Watts et al. found the linear isomer to be 30 kcal/mol more stable than the rhombic structure. This is in contrast to both the neutral species and the cation, for which the rhombus and the linear chain are nearly isoenergetic. The linear ground state of C4− has been studied using the first-order correlation orbital method (FOCO), SCF, MBPT, and coupled cluster techniques. Schmatz and Botschwina used large-scale coupled cluster calculations to determine values for the ground-state equilibrium bond lengths of 1.336 and 1.277 Å for the inner and outer bond lengths, respectively at the RCCSD(T)/256 cGTO level of theory. Symmetric stretch vibrational frequencies were predicted to be 2082.7 and 911.3 cm$^{-1}$ for $\nu_1$ and $\nu_2$, respectively. In addition, these authors calculated molecular parameters for three bound excited electronic states in the doublet manifold.

Figure 14 displays the $^2\Sigma_g^+\rightarrow^2\Pi_g$ electronic absorption spectra of mass-selected, even-numbered C4−–C20− deposited in Ne matrices at 5 K. (Reprinted with permission from ref 207. Copyright 1995 American Institute of Physics.)

**D. C4−**

The C4− cluster ion is predicted to be linear with a $^2\Pi_g$ ground electronic state. Using coupled cluster techniques, Watts et al. found the linear isomer to be 30 kcal/mol more stable than the rhombic structure. This is in contrast to both the neutral species and the cation, for which the rhombus and the linear chain are nearly isoenergetic. The linear ground state of C4− has been studied using the first-order correlation orbital method (FOCO), SCF, MBPT, and coupled cluster techniques. Schmatz and Botschwina used large-scale coupled cluster calculations to determine values for the ground-state equilibrium bond lengths of 1.336 and 1.277 Å for the inner and outer bond lengths, respectively at the RCCSD(T)/256 cGTO level of theory. Symmetric stretch vibrational frequencies were predicted to be 2082.7 and 911.3 cm$^{-1}$ for $\nu_1$ and $\nu_2$, respectively. In addition, these authors calculated molecular parameters for three bound excited electronic states in the doublet manifold.

Linear carbon cluster anions are particularly interesting because they possess excited electronic states that are stable with respect to electron auto-detachment. This makes them amenable to study by various electronic spectroscopy techniques. Maier and co-workers have measured electronic spectra for mass-selected carbon cluster anions deposited in Ne matrices in the C4−–C20− size range. Figure 14 displays the $^2\Pi_g\rightarrow^2\Pi_g$ spectra observed for these clusters. For C4−, the $^2\Pi_g\rightarrow^2\Pi_g$ vibrationless origin occurs at 21 896 cm$^{-1}$. A more recent study reported observations of the $^2\Pi_g\rightarrow^2\Pi_g$ transitions. Vibrationless origins for these transitions were measured to be 8293, 10 789, 26 069, and 28 868 cm$^{-1}$, respectively. Schäfer et al. measured the $^2\Pi_g\rightarrow^2\Pi_g$ emission spectra of mass-selected C4− in a Ne matrix to determine lower state fundamental vibrational frequencies. Their measurements of the $\nu_1$ and $\nu_2$ symmetric stretch frequencies of 2047 and 936 cm$^{-1}$, respectively, were in excellent agreement with the calculations of Schmatz and Botschwina. The $\nu_4$ symmetric bending frequency was also observed at 396 cm$^{-1}$.

Zhao et al. have studied the electronic spectra of gas-phase carbon cluster anions using resonant two-photon photodetachment (R2PD) techniques. Carbon cluster anions produced in a pulsed discharge/supersonic expansion source were mass selected and then photodetached using one and two-color R2PD. The C4− $^2\Pi_g\rightarrow^2\Pi_g$ vibronic spectrum of C4− was observed with a vibrationless origin of 21 872 cm$^{-1}$, which agreed well with the Ne matrix work. By minimizing the power broadening of the photodetachment transitions, Zhao et al. were able to resolve the rotational structure of the C4− $^2\Pi_g\rightarrow^2\Pi_g$ R2PD spectrum, making C4− the largest carbon cluster ion for which a rotationally resolved spectrum has been recorded. Figure 15 displays the experimental data, and Table 7 presents selected molecular parameters derived from the rotational analysis. Very
recently, Tulej et al. observed the \(^2\Pi_u - \chi^2\Pi_g\) and \(^3\Pi_u - \chi^2\Pi_g\) transitions in the gas phase using two-color photodetachment spectroscopy, with band origins of 25 989 and 28 717 cm\(^{-1}\), respectively.\(^{50}\)

As mentioned above, Szczepanski et al. have recently identified an infrared absorption band at 1699.8 cm\(^{-1}\), observed in an Ar matrix, as the \(v_3\) antisymmetric stretch of C\(_5\).\(^{236}\) This new assignment was based on isotopic substitution measurements as well as the different behavior observed for this band, with respect to the 1544 cm\(^{-1}\) band of neutral C\(_4\), after irradiating the matrix with an electron beam.

### E. C\(_4^+\)

In contrast to C\(_4^-\), there is very little information available about the C\(_4^+\) cation. Raghavachari performed HF and MP4 calculations on the structural isomers of C\(_4\) through C\(_6\) and their ions.\(^{216}\) His results for C\(_4^+\) predicted that, like the neutral, a linear chain and a rhombic isomer were nearly isoenergetic. The linear and rhombic isomers were found to possess \(^2\Pi_g\) and \(^2\Delta_u\) ground electronic states, respectively.

### VIII. C\(_5\)

#### A. Theory

The ab initio calculations of Raghavachari and Binkley were the first to consider relative energies for linear and cyclic isomers of C\(_5\).\(^{67}\) These calculations concluded that the ground-state structure was a \(\chi^2\Pi_g\) linear cumulene and was more stable than the lowest energy cyclic isomer by over 60 kcal/mol. More recent calculations support this prediction.\(^{217}\) C\(_5\) is the largest carbon cluster to be detected in an astrophysical source, having been observed in the circumstellar shell of the carbon star IRC+10216 via its \(v_3\) infrared absorption spectrum.\(^3\) A large body of theoretical work on C\(_5\) already existed prior to the Weltner and Van Zee review. Most of this work concentrated on the ground-state geometry, vibrational frequencies and intensities, and thermodynamic functions. More recent work has extended this treatment to higher levels of sophistication. Kurtz and Adamowicz calculated bond lengths and vibrational frequencies using first-order correlation orbitals along with coupled cluster techniques\(^{217}\) and at the MP2/6-31G* level.\(^{218}\) Botschwina and Sebald used the CEPA-1 (coupled electron pair approximation) approach with basis sets of contracted Gaussian-type orbitals.\(^{219}\) One of the purposes of this study was to calculate the frequency and intensity of the \(v_3\) mode, which had just been measured in the gas phase\(^{220}\) and in IRC+10216.\(^3\) On the basis of their intensity calculation, the authors recommended a value of \(5 \times 10^{13}\) cm\(^{-2}\) for the column density of C\(_5\) in IRC+10216.

Recently, Botschwina reported the largest scale calculation that has been performed on the C\(_5\) cluster to date.\(^{74}\) He used the CCSD(T) method with all electrons correlated and a very large basis set of 275 cGTO’s (cc-pVQZ) to calculate the ground-state geometry and the harmonic vibrational frequencies, SCF, MP2, and CCSD calculations were also performed using the same basis set for comparison. The estimated accuracy of bond lengths calculated at the CCSD(T)/cc-pVQZ level is 0.001 Å. For C\(_5\), Botschwina obtained 1.2896 and 1.2819 Å for the inner and outer equilibrium bond lengths, respectively. Force constants, the equilibrium rotational constant, and the frequencies of the \(v_1\) and \(v_2\) modes were also calculated.

Martin and Taylor calculated bond lengths, vibrational frequencies, and intensities at the CCSD(T)/cc-pVQZ level of theory.\(^{58}\) By scaling the calculated vibrational frequencies for several linear carbon chains with known experimental values, the authors predicted the frequency of the \(v_4\) antisymmetric stretch to be 1442.5 ± 28 cm\(^{-1}\), which is in agreement with a matrix study by Kranz and Graham.\(^{221}\)

#### B. Experiment

C\(_5\) was first identified by its 2164 cm\(^{-1}\) \(v_3\) infrared absorption transition in a rare gas matrix.\(^{199}\) In a
more recent study, Kranze and Graham assigned a much weaker Ar matrix absorption at 1446.6 cm$^{-1}$ to the $\tilde{v}_4$ antisymmetric stretch. Szczepanski et al. recently assigned Ar matrix absorptions at 2939.9 and 4327.8 cm$^{-1}$ to the $\tilde{v}_2 + \tilde{v}_3$ combination band and the $2\tilde{v}_3$ overtone, respectively. These assignments were based on similar annealing behavior with respect to the known $v_3$ transition and must be regarded as tentative, since isotopic substitution experiments were not performed. On the basis of the latter result, the authors obtained a value of $-0.1$ cm$^{-1}$ for the $x_{33}$ anharmonicity constant.

The $v_3$ absorption spectrum of C$_5$ was first detected in the gas phase simultaneously by Bernath et al., who observed a series of rovibrational transitions with a resolution of 0.010 cm$^{-1}$ in the carbon star IRC+10216, and in the laboratory by Heath et al. using a laser vaporization–supersonic cluster beam source to produce the clusters and infrared diode laser spectroscopy to record the spectra. These studies represented the first observation of rotationally resolved spectra for a polyatomic carbon cluster larger than C$_3$, and provided the most detailed structural information ever obtained for a cluster of this size. Figure 16 displays the C$_5$ absorption transitions observed toward IRC+10216. In their laboratory study, Heath et al. observed P- and R-branch transitions out to $J = 40$ with a precision in the frequency positions of $\sim 0.002$ cm$^{-1}$. From the relative intensities of the transitions, they estimated a rotational temperature of 10 K. Moazzen-Ahmadi et al. later observed the $v_3$ spectrum of C$_5$ using infrared diode laser spectroscopy of a hollow cathode acetylene discharge. The number of fundamental transitions observed by these authors was extended out to $J = 72$. Due to the high temperature of the acetylene discharge, several hot bands arising from low-frequency bending modes of $^{12}$C$_5$ were also observed. Hot bands that were analyzed were $(\tilde{v}_3 + \tilde{v}_7) - \tilde{v}_7$, $(\tilde{v}_3 + 2\tilde{v}_7) - 2\tilde{v}_7$, and $(\tilde{v}_3 + \tilde{v}_5) - \tilde{v}_5$. From the $l$-type doubling constants, $q_7$ and $q_5$, the authors estimated frequency positions of $118 \pm 3$ cm$^{-1}$ for the lowest $v_7$ bending frequency and $218 \pm 13$ cm$^{-1}$ for $v_5$. As with C$_4$, there is no evidence for exceptionally large amplitude bending motion in the lowest bending coordinate. Although perturbations to some of the rovibrational energy levels were observed, C$_5$ can generally be considered a well-behaved semirigid linear molecule with a cumulenic bonding configuration. Researchers from this same group also observed the $v_3$ band of the $^{13}$C$_5$ isotopomer.

Figure 17 displays photoelectron spectra observed for the odd-numbered C$_3$–C$_9$ clusters by Arnold et al. These authors measured the $2\nu_5$, $2\nu_6$, and $2\nu_7$, laboratory study, Heath et al. observed P- and R-branch transitions out to $J = 40$ with a precision in the frequency positions of $\sim 0.002$ cm$^{-1}$. From the relative intensities of the transitions, they estimated a rotational temperature of 10 K. Moazzen-Ahmadi et al. later observed the $v_3$ spectrum of C$_5$ using infrared diode laser spectroscopy of a hollow cathode acetylene discharge. The number of fundamental transitions observed by these authors was extended out to $J = 72$. Due to the high temperature of the acetylene discharge, several hot bands arising from low-frequency bending modes of $^{12}$C$_5$ were also observed. Hot bands that were analyzed were $(\tilde{v}_3 + \tilde{v}_7) - \tilde{v}_7$, $(\tilde{v}_3 + 2\tilde{v}_7) - 2\tilde{v}_7$, and $(\tilde{v}_3 + \tilde{v}_5) - \tilde{v}_5$. From the $l$-type doubling constants, $q_7$ and $q_5$, the authors estimated frequency positions of $118 \pm 3$ cm$^{-1}$ for the lowest $v_7$ bending frequency and $218 \pm 13$ cm$^{-1}$ for $v_5$. As with C$_4$, there is no evidence for exceptionally large amplitude bending motion in the lowest bending coordinate. Although perturbations to some of the rovibrational energy levels were observed, C$_5$ can generally be considered a well-behaved semirigid linear molecule with a cumulenic bonding configuration. Researchers from this same group also observed the $v_3$ band of the $^{13}$C$_5$ isotopomer.

Figure 17 displays photoelectron spectra observed for the odd-numbered C$_3$–C$_9$ clusters by Arnold et al. These authors measured the $2\nu_5$, $2\nu_6$, and $2\nu_7$,
bending transitions and the ν2 symmetric stretch of C5. From these measurements, they estimated the following vibrational frequencies: ν5 = 222 cm⁻¹, ν6 = 512 cm⁻¹, ν7 = 101 cm⁻¹, and ν2 = 798 cm⁻¹, with uncertainties in the frequency positions of 45 cm⁻¹. The ν5 and ν7 frequencies are in agreement with the estimated values of Moazzen-Ahmadi et al.222 Kitsopoulos et al.223 later measured vibrational frequencies with much higher precision by selectively detecting only the zero kinetic energy (ZEKE) electrons as a function of the photodetachment frequency.224

Ground-state vibrational frequencies for both the anion and the neutral were obtained from this study. For the neutral, the authors obtained the following vibrational frequencies: ν2 = 779 cm⁻¹, ν5 = 216 cm⁻¹, ν6 = 535 cm⁻¹, and ν7 = 107 cm⁻¹ with uncertainties of about 5 cm⁻¹. Evidence for an excited electronic state of neutral C5 was obtained as well and will be discussed below. Experimental and theoretical molecular parameters for C5 are presented in Table 8.

### C. Excited Electronic States

The electronic spectrum of linear C5 is analogous to that of C3. A 3Πu–XΣg⁺ transition was predicted to occur at 428 nm by Kolbuszewski using MRD-CI/5s3p1d calculation compared to the 405-nm transition for C3. This transition was recently measured by Forney et al. from mass-selected C5 clusters trapped in solid Ne.167 The observed band origin was 19599 cm⁻¹ (510.2 nm). Kolbuszewski also predicted a 1Πg state at 2.85 eV and a 3Πg state lying 0.8 eV lower in energy.225 No transitions involving these energy levels have been observed experimentally. Kitsopoulos et al. observed a series of peaks in their threshold photodetachment experiment 0.26 eV above the origin band.224 These peaks were tentatively assigned to transitions to a low-lying 3Πg state, which was consistent with the selection rules of negative ion photodetachment and with the line width broadening observed when compared to the ground-state transitions. However, this assignment is in conflict with the calculations of Kolbuszewski who predicted a term energy of 2.03 eV for this state.225

### D. C5⁻

The C5⁻ carbon cluster anion is linear with a 2Πu ground electronic state.176,226 Equilibrium bond lengths of 1.309 and 1.269 Å were calculated at the ROHF/DZP level of theory for the inner and outer bond lengths, respectively.176 C5⁻ has been studied experimentally using anion photoelectron spectroscopy,41 zero electron kinetic energy (ZEKE) spectroscopy,224 multiphoton photodetachment spectroscopy,47 gas-phase ion mobility studies,227 and infrared177,228 and electronic absorption spectroscopy in rare gas matrices.

Kitsopoulos et al. observed a hot band transition in their ZEKE spectra of C5⁻ that they attributed to the ν7 antisymmetric bending vibration, measured to be 200 ± 50 cm⁻¹.224 Until very recently, this was the only measurement of a fundamental vibration in the electronic ground state of C5⁻. Two groups have recently reported observations of an antisymmetric stretch mode of C5⁻ trapped in rare gas matrices. Szymczynski et al. assigned a transition at 1831.8 cm⁻¹ in an Ar matrix, observed after irradiating the matrix with an electron beam, to the ν7 vibration (see Figure 10).177 This assignment was made on the basis of density functional theory calculations performed by the authors. Freytag et al. observed this same band from mass-selected C5⁻ deposited in a Ne matrix. In this case, the transition frequency was measured to be 1822.3 cm⁻¹.228

It has long been recognized that the even-numbered carbon cluster anions possess bound excited electronic states, due to the high electron affinities

### Table 8. Molecular Parameters of X 1Σg⁺ C5⁻

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<th>theory</th>
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² Numbers in parentheses are uncertainties in the last digits. Numbers in brackets are IR intensities [km/mol].³ Infrared diode laser spectroscopy.222 ⁴ CCSD(T)/275sCSTOs.²⁴ ⁵ CCSD(T)/cc-pVQZ.⁴³ ⁶ ZEKE spectroscopy.224 ⁷ Ar matrix.¹³⁸ ⁸ BLYP/cc-pVDZ.⁶² ⁹ Ar matrix.²¹ ¹ Estimated from the l-type doubling constants.²²² ¹¹ DFT(BLYP).⁶⁰ ¹² Infrared diode laser spectroscopy.²²³
of the linear triplets.\textsuperscript{175,176,210} Recent experimental studies have revealed that the odd-numbered anions also possess bound electronic states,\textsuperscript{47,49,214} despite earlier theoretical predictions to the contrary.\textsuperscript{226} Ohara et al. accomplished the first observation of a gas-phase electronic spectrum of a polyatomic carbon cluster anion.\textsuperscript{47} These authors observed two broad peaks in their resonance-enhanced multiphoton photodetachment spectrum of C$_5^-$ produced in a laser vaporization–supersonic expansion source, which were assigned as transitions to the $\Delta^2\Pi_0$ excited electronic state. The $\Delta^2\Pi_0 \rightarrow \chi^2\Pi_u$ spectrum was also measured by Forney et al. from mass-selected C$_5^-$ in a Ne matrix.\textsuperscript{214} The band origin was measured to be 20 200 cm$^{-1}$ (495.1 nm). The line widths observed for these transitions was about 0.2 cm$^{-1}$, which was narrower than the gas-phase line widths by about a factor of 35. Forney et al. also observed a band system assigned as the $\Pi^2\Pi_0 \rightarrow \chi^2\Pi_u$ spectrum of C$_5^-$;\textsuperscript{204} The observed band origin was 27 847 cm$^{-1}$ (359.1 nm).

E. C$_6^+$

As with C$_4^+$, there is very little structural and spectroscopic information available for C$_6^+$. Raghavachari found two low-lying electronic states for the linear ground state—a $2\Sigma_u^+$ state and a $2\Pi_g$ state using HF and MP4 theoretical techniques.\textsuperscript{216} He found the $2\Sigma_u^+$ state to be lower in energy by 0.4 eV.

IX. C$_6$

A. Theory

Like C$_4$, C$_6$ is predicted to exist as two low-energy structural isomers, a cumulenic linear $3\Sigma_u^+$ form and a planar $1\Delta_g$ monocyclic ring. The lowest energy cyclic structure is a distorted hexagon ring of D$_{3h}$ symmetry. (See Figure 1.) As expected on the basis of experience with C$_4$, the calculated relative energies of the two isomers are extremely sensitive to the ab initio technique. The first high-level ab initio calculation to address relative isomer energies of C$_6$ were those of Raghavachari et al., who performed calculations at several different levels of theory, the highest one being MP4/6-31G*.\textsuperscript{67,229} These authors studied energies of the linear cumulene and acetylene structures and four different cyclic isomers, including a symmetric D$_{3h}$ ring, a distorted D$_{3h}$ ring and the chair conformation. From a vibrational analysis, they found that the two linear structures and the D$_{3h}$ structures were minima on the potential energy surface, while the remaining isomers represented saddle points. The $3\Sigma_u^+$ structure was found to be the lowest energy linear form but was about 19.3 kcal/mol higher in energy than the D$_{3h}$ isomer. Parasuk and Almlof studied similar structures using MCSCF and MRCI methods.\textsuperscript{69} These calculations concluded that the cumulenic chain was more stable than the D$_{3h}$ isomer by over 40 kcal/mol, in stark contrast to the earlier results of Raghavachari et al. Even the polyacetylene structure, which was less stable than the cumulene by about 20 kcal/mol, was more stable than the ring.

Two recent theoretical studies addressed the discrepancies between the calculations of Raghavachari et al. and those of Parasuk and Almlof. Pless et al. performed a detailed investigation of the effect of electron correlation on the energy separation between the linear and cyclic isomers.\textsuperscript{73} These calculations were performed using the MRD-CI, CASPT2, and CCD methods with ANO basis functions. The authors found that correlation of all 24 valence electrons was critical for obtaining reliable relative energies. In Parasuk and Almlof’s study, only 10 valence electrons were correlated at the MR-CI level. Furthermore, the theoretical technique used to take correlation effects into account is also critical. Very sophisticated techniques, like CCSD(T) and MRD-CI that take into account high order correlation effects, must be employed for clusters of this complexity. At the MRD-CI level, Pless et al. predicted that the D$_{3h}$ structure is the ground state, with the linear cumulene lying 7 kcal/mol higher in energy. The symmetric D$_{3h}$ structure was found to be a saddle point, lying 5 kcal/mol above the ground state. Hutter and Lüthi performed a similar study using CCSD(T) calculations with ANO basis functions.\textsuperscript{72} These authors also studied electron correlation effects and arrived at the same conclusion reached by Pless et al., that all valence electrons must be correlated at a high level of theory to achieve convergence of the relative energies. At the CCSD(T) level, the D$_{3h}$ structure was again found to be the ground state by 10.7 kcal/mol over the cumulene.

Schmatz and Botschwina performed large-scale calculations on the ground electronic state parameters of linear C$_6$ in conjunction with their ab initio study of the excited electronic states of linear C$_6^-$.\textsuperscript{75} Open-shell coupled cluster methods, which take into account triple excitations, were used with a basis set of 207 cGTO’s. At the RCCSD(T) level of theory, these authors obtained the following equilibrium bond lengths for linear C$_6$: 1.2738, 1.2861, and 1.3011 Å for the inner, middle, and outer bonds, respectively. Martin and Taylor included the C$_6$ cluster as part of their study of the structures and vibrational spectra of C$_2-$C$_9$.\textsuperscript{58} C$_6$ calculations were performed at the CCSD(T) level using cc-pVDZ and cc-pVTZ basis sets. The authors found the energy splitting between the linear and cyclic isomers to be 13 ± 2 kcal/mol, also in favor of the ring at the CCSD(T)-cc-pVTZ level. On the basis of their vibrational analysis, the authors predicted that the most intense infrared active vibrational mode of cyclic C$_6$ should occur in the region of 1700–1800 cm$^{-1}$. Matrix absorption peaks at 1695 and 1715 cm$^{-1}$ were suggested as possible candidates for this mode. The former prediction was recently confirmed experimentally, as will be discussed below. For linear C$_6$, the infrared spectrum was dominated by a very intense antisymmetric stretch ($\nu_4$) with an unscaled CCSD(T)-cc-pVDZ frequency of 991 cm$^{-1}$, while the weaker $\nu_5$ antisymmetric stretch band was predicted to occur at 1197 cm$^{-1}$. Two infrared active bending transitions with very weak intensities were predicted to occur in the far-infrared region.
B. Experiment

1. The Cyclic Isomer

Zajfman et al. reported evidence for a nonlinear isomer of C₆, based on the observation that significant electron photodetachment cross sections for C₆⁻ were measured at energies below the known electron affinity of the linear isomer. This observation was interpreted as a linear anion to nonlinear neutral photodetachment transition. Similar results were also obtained from C₄⁻→C₈⁻ photodetachment cross section measurements. Recently, however, Neumark and co-workers have shown that these apparently low photodetachment cross sections were most likely the result of multiphoton processes. These authors performed a study of the spectroscopy and electron detachment dynamics of C₄⁻, C₆⁻, and C₈⁻ using resonant multiphoton detachment spectroscopy. They found that, for all three ions, efficient resonant multiphoton detachment occurred at the low photon energies reported by Zajfman et al.

Two groups recently reported the first spectroscopic identification of a small cyclic carbon cluster. Presilla-Marquez et al. and Wang et al. have simultaneously and independently assigned an infrared absorption transition at 1695 cm⁻¹ to the v₁ fundamental transition of cyclic C₆ trapped in an Ar matrix at 10 K. This assignment was supported by density functional theory calculations and by good agreement between the observed and calculated frequency shifts of the ¹³C-substituted isotopomers. This is a very significant result, given the great importance of experimentally characterizing the cyclic isomers of small carbon clusters. It is hoped that these initial measurements will eventually lead to a more detailed characterization of cyclic C₆ by high-resolution gas-phase spectroscopy.

2. The Linear Isomer

The Ï\(^g\) form of C₆ was first identified by its ESR spectrum in an Ar matrix. Later, Vala et al. used isotopic substitution techniques to assign an Ar matrix absorption at 1952 cm⁻¹ to the v₂(e') fundamental transition of cyclic C₆ trapped in an Ar matrix at 10 K. This assignment was supported by density functional theory calculations and by good agreement between the observed and calculated frequency shifts of the ¹³C-substituted isotopomers. This is a very significant result, given the great importance of experimentally characterizing the cyclic isomers of small carbon clusters. It is hoped that these initial measurements will eventually lead to a more detailed characterization of cyclic C₆ by high-resolution gas-phase spectroscopy.

![Figure 18. Experimental data and a simulated stick spectrum showing rovibrational transitions and triplet fine structure of the Ï\(^e\) antisymmetric stretch of linear C₆. The rotational temperature was 25 K. A laser vaporization-supersonic molecular beam source was used to produce the clusters, and a tunable diode laser spectrometer was used to record the spectra. Peaks labeled with asterisks are unassigned transitions. (Reprinted from ref 236. Copyright 1993 Taylor & Francis.)](image)
Table 9. Molecular Parameters of X^2Σ_u^+ C_6

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</tbody>
</table>

² Numbers in parentheses are uncertainties in the last digits. Numbers in brackets are calculated IR intensities [km/mol].

a Infrared diode laser spectroscopy.²³⁶ b ESR spectroscopy in a Ne matrix.²³²,²³³ c ESR spectroscopy in an Ar matrix.²³²,²³³ d Inner, middle, and outer (respectively) equilibrium bond lengths calculated at the RCCSD(T)/204cGTO level.²³⁷ e TZEKE spectroscopy.²²³ f CCSD(T)/cc-pVDZ.³⁸ g RCCSD(T)/204cGTO.²⁵ h Photoelectron spectroscopy.⁴² i Ar matrix.²³⁴,²³⁵ j B3LYP/cc-pVDZ.⁶⁰ k Ar matrix.²³⁵ l MP2/6-31G*.²⁴⁴

Cluster to undergo large amplitude motion in its lowest-frequency bending coordinate. Like C₃, C₆ possesses a τ₀ HOMO, as opposed to C₄, and C₅ which possess τ₁ HOMO’s. To date, no rotationally resolved spectra of C₆ that sample the lowest frequency bending mode have been assigned. Therefore, it is not currently possible to definitively characterize the bending dynamics. However, for very floppy molecules, the centrifugal distortion tends to be unusually large due to the high density of bending vibrational states that can interact with the antisymmetric stretch through the Coriolis effect. For C₆, the centrifugal distortion constant, D₀, is about 1 order of magnitude larger than expected for a semirigid molecule of this size, which may be an indication of a floppy bending potential. There is no evidence for quasi-linearity in the bending potential upon excitation of the antisymmetric stretch, as is the case for C₃.

The symmetric stretch vibrations of C₆ were assigned at low resolution using anion photoelectron spectroscopy (see Figure 12),⁴¹ and at higher resolution using threshold photodetachment spectroscopy by Neumark and co-workers.²³⁷ The threshold photodetachment spectra were characteristic of linear geometries for both the anion and the neutral. The following symmetric stretch frequencies were assigned: v₁ = 2061 cm⁻¹, v₂ = 1322 cm⁻¹, and v₃ = 489 cm⁻¹. Uncertainties in these frequencies were ±10 cm⁻¹. The latter two assignments are in conflict with the recent coupled cluster results of Schmatz and Botschewia.⁷⁵ Their force field calculations at the RCCSD(T) level predicted the harmonic frequencies of v₂ and v₃ to occur at 1683 and 649 cm⁻¹, respectively. Assignment of the v₂ + v₃ absorption in an Ar matrix by Szczepanski et al., which implies a value for v₂ of 1665.8 cm⁻¹, supports this theoretical prediction.²¹³ Hutter et al. suggested that the peak assigned to v₂ might be due to a low-lying ³Π₉ state.⁷² In more recent experiments, Xu et al. measured much more detailed photoelectron spectra for C₆⁻ than had been observed previously.⁴² Transitions that were separated from the origin by 1694 ± 50 and 637 ± 50 cm⁻¹ were observed and assigned to v₂ and v₃, in better agreement with theoretical predictions.

C. Excited Electronic States

Liang and Schaefer calculated term energies for the low-lying ¹Σ₉ and ¹(ΣΔ) states of cumulenic linear C₆.⁸⁶ At the CISD/DZP level, with all valence electrons correlated, including Davidson’s correction, the term energy of the ¹Σ₉ state was 0.15 eV. Parasuk and Almlöf also predicted the relative energy of the ¹Π₉ state using CASSCF and configuration interaction methods.⁶⁹ At the CISD/ANO level, with 14 valence electrons correlated and with the inclusion of Davidson’s correction, the authors predicted the ¹Σ₉ state to lie at 0.19 eV. The term energy of the ¹Π₉ state was recently measured by Xu et al., using photoelectron spectroscopy of C₆⁻, to be 0.166 ± 0.015 eV,⁴² in excellent agreement with the theoretical predictions. Other low-lying electronic states observed by these authors were the ²Σ_u⁻ state and the ³Π_u state, with term energies of 0.85 ± 0.02 and 1.10 ± 0.02 eV, respectively.

Forney et al. measured ²Σ_u⁻-X²Σ_u⁻ vibronic transitions as part of their study of mass selected linear carbon clusters and anions trapped in solid Ne (see Figure 13).²⁰⁶ The term energy of the ³Σ_u⁻ state of neutral C₆ was 19558 cm⁻¹. The 1952 cm⁻¹ vibrational absorption of C₆ was observed simultaneously. Three of the bands assigned to linear C₆ in this work at 511, 462, and 449 nm had been tentatively assigned to linear C₄ and C₂⁻ in previous studies by Graham et al.²³⁸ and Szczepanski and Vala.²⁰⁵
D. \( C_6^- \)

A number of theoretical studies have been reported that characterized the \( ^2\Pi_u \) ground state and several excited electronic states of linear \( C_6^- \).\(^{75,175,176}\) The most sophisticated of these was the large-scale coupled cluster study of Schmatz and Botschwina.\(^{75}\) These authors predicted values for the equilibrium bond lengths of 1.252, 1.325, and 1.275 Å for the inner, middle, and outer bond lengths, respectively, on the basis of calculations performed at the RCCSD(T) level. Raghavachari studied the relative isomer energies of linear and cyclic \( C_6^- \) using HF and MP4 techniques.\(^{216}\) He found the linear isomer to be more stable by about 1.4 eV. The ion mobility of \( C_6^- \) through a He drift cell was characteristic of a single linear isomer.\(^{227,239}\)

Experimental techniques that have been used to study \( C_6^- \) are negative ion photoelectron spectroscopy,\(^{41,42}\) ZEKE spectroscopy,\(^{237}\) resonant two-photon photodetachment,\(^{48}\) gas-phase ion mobility measurements,\(^{227,239}\) infrared,\(^{177,228,240}\) and electronic\(^{226,207,212}\) absorption spectroscopy of \( C_6^- \) trapped in rare gas matrices, and matrix resonance Raman spectroscopy.\(^{240}\)

Several fundamental vibrations in the \( C_6^- \) ground electronic state have been assigned. Szczepanski et al. measured the \( v_1, v_2, \) and \( v_3 \) symmetric stretch modes to be 2086, 1775, and 634 cm\(^{-1}\), respectively using resonance Raman spectroscopy of \( C_6^- \) trapped in an Ar matrix.\(^{240}\) These assignments were supported by density functional theory calculations and isotopic shift measurements. The \( v_4 \) antisymmetric stretch was observed at 1936.7 cm\(^{-1}\) in an Ar matrix (see Figure 10)\(^{227,240}\) and 1938.5 cm\(^{-1}\) in Ne\(^{228}\) by infrared absorption spectroscopy.

Electronic absorption spectra of \( C_6^- \) were first observed by Forney et al. by trapping the mass-selected ions in a Ne matrix (see Figure 14).\(^{206}\) The \( ^2\Pi_u \rightarrow \Pi_{\alpha\beta} \) spectrum was observed with a band origin of 16458 cm\(^{-1}\) (607.6 nm). Zhao et al. measured this same band in the gas phase using two-photon photodetachment.\(^{48}\) The observed band origin was 16476 cm\(^{-1}\). Freivogel et al. have recently reported new electronic absorption spectra of mass-selected \( C_6^- \) trapped in a Ne matrix.\(^{240}\) These spectra were assigned as the \( \Pi_{\alpha\beta} \rightarrow X \Pi_{\alpha\beta} \) band, \( 2\Pi_{\alpha\beta} \rightarrow X \Pi_{\alpha\beta} \), and \( 3\Pi_{\alpha\beta} \rightarrow X \Pi_{\alpha\beta} \) bands, with band origins at 9352, 20064, and 22517 cm\(^{-1}\), respectively.

E. \( C_6^+ \)

Raghavachari's HF and MP4 calculations predicted a linear \( ^2\Pi_u \) ground state for \( C_6^+ \), although he could not give a reliable estimate for the relative stability of the cyclic isomer at this level of theory.\(^{216}\) von Helden et al. performed ROMP2 and SD-CI calculations on linear and planar monocyclic ring isomers of carbon cluster cations, including \( C_6^+ \).\(^{243}\) These calculations predicted that the linear and cyclic isomers are essentially isoenergetic, with the latter level of theory favoring the chain, and the former favoring the ring. Measurements of the ion mobility of \( C_6^+ \) ions through a high-pressure He drift cell were consistent with a single linear isomer.\(^{242,243}\)

X. \( C_7 \)

A. Theory

The most stable form of \( C_7 \) is predicted to be a linear cumulene with a \( ^2\Sigma^+ \) ground electronic state, as is also the case for \( C_5^- \). Martin et al. calculated structures and vibrational spectra of linear \( C_5^- \) clusters in an attempt to assign some of the unknown infrared matrix absorptions.\(^{244}\) Two intense antisymmetric stretch bands were found for \( C_7 \). At the RHF/6-31G* level these bands occurred with harmonic frequencies of 2281 and 2132 cm\(^{-1}\), with the largest intensity in the higher frequency band. On the basis of these calculations, the authors suggested that two well-correlated matrix absorptions at 1893 and 2128 cm\(^{-1}\) belonged to the \( v_5 \) and \( v_4 \) bands of linear \( C_7 \), respectively. These assignments were confirmed when both bands were observed in the gas phase as will be discussed below.

von Helden et al. performed ab initio calculations to study the structural isomers of \( C_7 \) and its ions.\(^{245}\) At the MP2 level, these authors found a \( C_7 \) planar ring isomer to be a local minimum of neutral \( C_7 \), lying about 19 kcal/mol above the linear ground state. Slanina et al. also studied the isomers of \( C_7 \) in an earlier study.\(^{246}\) These authors obtained a cyclic minimum lying 17 kcal/mol above the linear isomer. Finally, Martin et al. studied the isomerization of \( C_7 \) using coupled cluster and density functional methods.\(^{247}\) They obtained a relative energy of 14 kcal/mol in favor of the linear chain at the CCSD(T)/cc-pVQZ level of theory.

The highest level calculations to be performed on the linear ground state of \( C_7 \) are those of Schmaltz and Botschwina, who used open-shell coupled cluster techniques to study the \( \Pi \) \( \rightarrow \Sigma \) ground state and the \( \Pi \) \( \rightarrow \Pi \) state of \( C_7 \).\(^{57}\) Bond lengths calculated at the neutral cluster at the MC-CI level were 1.290, 1.286, and 1.272 Å for the outer, middle, and inner bonds, respectively. The authors calculated an anharmonic force field involving the symmetric stretch vibrations for both the anion and the neutral. These data, along with the calculated electron affinity, were used to reproduce the photoelectron spectrum measured by Arnold et al.\(^{41}\)

Martin and Taylor used CCSD(T) methods with a cc-pVQZ basis set to obtain bond lengths and harmonic vibrational frequencies of the stretching modes.\(^{58}\) Bond lengths calculated at this level tended to be too long by 0.01–0.02 Å, although harmonic vibrational frequencies were adequately reproduced. The infrared spectrum was dominated by a very intense antisymmetric stretch \( (\nu_4) \), with a less intense antisymmetric stretch occurring at lower frequency \( (\nu_5) \).

B. Experiment

The linear \( C_7 \) cluster was first detected in a solid Ar matrix via its infrared vibrational spectrum. Absorption bands at 1893 and 2128 cm\(^{-1}\) were observed in the early work of Thompson et al., who recognized that the two bands were highly correlated from their annealing behavior, although the very
complex isotopic substitution pattern could not be analyzed at that time. The authors concluded that the absorber was a large linear chain and tentatively assigned the bands to C$_9$. Martin et al. later suggested a reassignment of these bands to $v_5$ and $v_4$ of C$_7$ as has already been discussed. These bands were reevaluated in recent matrix work by Kranze et al. to further characterize the sensitivity of vibrational frequency calculations to $^{13}$C isotope substitution. Szczepanski et al. assigned Ar matrix absorptions at 2709.7 and 4255.6 cm$^{-1}$ to the $v_3 + v_4$ combination band and the 2$v_4$ overtone, respectively. A value of $x_{4u} = -0.2$ cm$^{-1}$ was obtained for the anharmonicity constant of the $v_4$ mode.

C$_7$ was first studied in the gas phase by Heath et al., who observed the $v_4$ rovibrational spectrum using tunable infrared diode laser spectroscopy of a supersonic cluster beam. These authors measured rovibrational transitions out to $J = 42$ with an estimated rotational temperature of 10 K. The band origin at 2138.1951 cm$^{-1}$ confirmed the assignment of the 2128 cm$^{-1}$ matrix absorption. A later study by Heath and Saykally extended the number of observed fundamental transitions out to $J = 64$. In addition, adjustments in the experimental conditions for producing the clusters in the laser vaporization source permitted the observation of hot band transitions, whose signal-to-noise ratio was about a factor of 10 weaker than the fundamental transitions. These hot bands were assigned to the $(v_4 + v_{11}) - v_{11}$ and the $(v_4 + 2v_{11}) - 2v_{11}$ transitions, where $v_{11}$ is due to bending about the central carbon atom and is the lowest frequency vibration. P- and R-branch transitions out to $J = 11$ were measured for the $(v_4 + v_{11}) - v_{11}$ band, while for the $(v_4 + 2v_{11}) - 2v_{11}$ band only R-branch transitions out to $J = 20$ in the $l = 0$ component were observed. Figure 19 displays experimental data showing $v_4$ fundamental and $(v_4 + v_{11}) - v_{11}$ hot bands transitions along with a calculated stick spectrum. Heath et al. later measured rovibrational transitions of the $v_5$ fundamental band out to $J = 42$. The band origin was 1898.3758 cm$^{-1}$, which also confirmed the matrix assignment of the 1893 cm$^{-1}$ band. The relative intensity of $v_5$ was found to be about 5–7 times weaker than that of the $v_4$ band. Molecular parameters resulting from analysis of the observed spectra can be found in Table 10.

C$_7$ possesses a filled $x_u$ HOMO, which makes this molecule a candidate for extremely large amplitude bending motion. From the high-resolution spectroscopy data, rotational constants for the ground vibrational state and the first two excited $v_{11}$ bending states were obtained. The rotational constant increased by 9.3% upon excitation of the first excited bending level, and 22% when the second level was excited. This extremely large increase in the rotational constant upon bending excitation is unprecedented for a strongly bound linear molecule. For example, excitation of the lowest frequency bending mode of C$_5$ results in a corresponding increase of the rotational constants of only 0.36% and 0.70% for the first two excited states. The enormous increase in the rotational constant observed for C$_7$ results from large amplitude motion in the $v_{11}$ bending coordinate.

Figure 19. Rovibrational transitions of the $v_4$ antisymmetric stretch and the $(v_4 + v_{11}) - v_{11}$ hot band of C$_7$. The clusters were produced in a laser vaporization—supersonic expansion source, and the spectra were recorded using a tunable diode laser spectrometer. (Reprinted from ref 250. Copyright 1991 American Institute of Physics.)

Theoretical calculations predict a harmonic bending frequency of $v_{11}$ that is in the far-infrared region of the spectrum. However, the true bending potential is likely to be very anharmonic, which would probably result in a much lower frequency bending mode than the calculations predict. Further evidence for unusual behavior in the vibrational dynamics of C$_7$ arose from the centrifugal distortion parameters. These constants were large and negative for both the ground state and the excited state, which may be due to Coriolis perturbations occurring between the stretching and bending modes. There was no evidence for quasilinearity in the potential surface of C$_7$ however, since excitation of the antisymmetric stretch fundamental resulted in the expected decrease of the rotational constant.

The negative ion photoelectron spectrum of C$_7$ was difficult to interpret due to the large spectral congestion that resulted from the low-frequency bending modes and the lower instrument resolution at higher electron kinetic energies (see Figure 17). Only two vibrational modes of the neutral were tentatively assigned, the $v_3$ symmetric stretch at 548 ± 90 cm$^{-1}$ and the $v_7$ bend at 496 ± 110 cm$^{-1}$. This assignment of the $v_3$ symmetric stretch was consistent with the
Table 10. Molecular Parameters of X1\(\Sigma^+_u\) C\(_7^-\)

<table>
<thead>
<tr>
<th>parameter</th>
<th>experiment</th>
<th>theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_0) (cm(^{-1}))</td>
<td>0.030613(14)(^a)</td>
<td>1.272 1.286 1.290(^c)</td>
</tr>
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<td>(D_0) (10(^{-7}) cm(^{-1}))</td>
<td>-0.233(85)(^b)</td>
<td>2154(^d) 2163(^d)</td>
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<tr>
<td>(r_0) (Å)</td>
<td>1.2800(6)(^b)</td>
<td>1547(^d) 1557(^d)</td>
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<tr>
<td>(v_1(\omega_0)) (cm(^{-1}))</td>
<td>2138.3152(5)(^b)</td>
<td>569(^d) 572(^d)</td>
</tr>
<tr>
<td>(v_2(\omega_0)) (cm(^{-1}))</td>
<td>548(90)(^d)</td>
<td>2015(^d) 2128(^d)</td>
</tr>
<tr>
<td>(v_3(\omega_0)) (cm(^{-1}))</td>
<td>1896.3758(8)(^d)</td>
<td>1914(^d) 1988(^d) 1307(^d)</td>
</tr>
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<td>(v_4(\omega_0)) (cm(^{-1}))</td>
<td>1893(^d)</td>
<td>1999(^d) 2020(^d)</td>
</tr>
<tr>
<td>(v_5(\omega_0)) (cm(^{-1}))</td>
<td>0.030556(15)(^d)</td>
<td>0.16(11)(^d)</td>
</tr>
<tr>
<td>(v_6(\omega_0)) (cm(^{-1}))</td>
<td>496(110)(^d)</td>
<td>1077(^d) 1119(^d) 16(^d)</td>
</tr>
<tr>
<td>(v_7(\omega_0)) (cm(^{-1}))</td>
<td>0.033583(40)(^d)</td>
<td>574(^d)</td>
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<tr>
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<td>190(^d)</td>
</tr>
<tr>
<td>(D(10^{-7} \text{ cm}^{-1}))</td>
<td>708 [6 x 2](^d)</td>
<td>293 [6 x 2](^d)</td>
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<td>(v_1(\omega_0)) (cm(^{-1}))</td>
<td>80 [10 x 2](^d)</td>
<td>289(^d)</td>
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<tr>
<td>(v_2(\omega_0)) (cm(^{-1}))</td>
<td>0.030496(14)(^d)</td>
<td>1893(^d)</td>
</tr>
<tr>
<td>(v_3(\omega_0)) (cm(^{-1}))</td>
<td>-0.251(91)(^d)</td>
<td></td>
</tr>
<tr>
<td>(v_4(\omega_0)) (cm(^{-1}))</td>
<td>1.2800(6)(^b)</td>
<td></td>
</tr>
<tr>
<td>(r_0) (Å)</td>
<td>1.279(^a)</td>
<td>1.307(^d) 1.279(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Numbers in parentheses are uncertainties in the last digits. Numbers in brackets are calculated IR intensities [km/mol].
\(^b\) Infrared diode laser spectroscopy.
\(^c\) Inner, middle, and outer equilibrium bond lengths calculated at the RCCSD(T)/6-31G** level.
\(^d\) RCCSD(T)/6-311+G(d,p) calculations.

C. Excited Electronic States

The \(1\Pi_u - X\Sigma^+_u\) transition of C\(_7^-\) that is analogous to the 405-nm C\(_5^-\) band was predicted by Kolbuszewski to occur at 469 nm at the MRD-CI/5s3p2d level.225

The excitation energy of the \(1\Sigma^+_u - X\Sigma^+_u\) state was predicted to be 223.8 nm. These bands were observed by Forney et al. by electronic absorption spectroscopy of mass selected C\(_7^-\) trapped in a Ne matrix,257 which they assigned as the band origin of the \(A^1\Pi_u - X^1\Pi_g\) band.214

There have been several reports of the detection of metastable carbon cluster dianions as small as C\(_7^2^-\).258-260 Earlier theoretical studies had found C\(_8^2^-\) to be the smallest stable dianion with a linear chain structure.176-264 However, more recent calculations have predicted that a trigonal planar isomer of C\(_7^2^-\) is stable with respect to electron loss.255,256

D. C\(_7^-\)

The C\(_7^-\) ion is a linear chain with a \(3\Pi_g\) ground electronic state.57,176,245 Schmaltz and Botschwa calculated the equilibrium bond lengths at the RCCSD(T)/238cGTO level to be 1.279, 1.307, and 1.279 Å for the inner, middle, and outer bond lengths, respectively.57 C\(_7^-\) has been studied experimentally using anion photoelectron spectroscopy,44 resonance-enhanced multiphoton ionization mass spectrometry (REMPI),49 ion mobility measurements,227,228 and infrared27,228 and electronic24 ion mobility studies. Ion mobility studies revealed no evidence for a cyclic isomer of C\(_7^-\)227,228

Szczepeński et al. tentatively assigned a vibrational transition observed at 1734.8 cm\(^{-1}\) in an Ar matrix to the \(v_5\) antisymmetric stretch of C\(_7^-\) (see Figure 10).177 Their density functional theory calculations supported this assignment. This same transition was observed by Freyvogel et al. at 1736.4 cm\(^{-1}\) from mass-selected C\(_7^-\) deposited in a Ne matrix,228 confirming the assignment of Szczepeński et al. Ohara et al. observed REMPI spectra of gas-phase C\(_7^-\), C\(_8^-\), and C\(_{11}^-\).49 They measured an electronic band of C\(_7^-\) whose band origin occurred at 15950 cm\(^{-1}\). Forney et al. recently observed this same transition at 15954 cm\(^{-1}\) from mass-selected C\(_7^-\) in a Ne matrix, which they assigned as the band origin of the \(A^1\Pi_u - X^1\Pi_g\) band.214

E. C\(_7^+\)

Ion–molecule reactions between carbon cluster cations and D\(_2\), O\(_2\), HCN, and small hydrocarbons, studied by ICR/FTMS, revealed that C\(_7^+\), C\(_8^+\), and C\(_9^+\) existed in two different isomeric forms—a reactive form, postulated to be linear, and an unreactive form, presumed to be cyclic.257-259 These assumptions were confirmed by the gas-phase ion chromatography experiments of von Helden et al.241-243,260 Mass-selected carbon cluster ions were passed through a high-pressure (1-5 Torr) He drift cell under the influence of a 2–20 V/cm electric field. Temporal separation of different structural isomers occurred in the drift cell, due to the dependence of the ion mobilities on the geometric structures. Cyclic isomers possess higher mobilities than linear isomers, so that the cyclic clusters moved through the cell at a faster rate. A short pulse of ions is injected into the drift cell, and the arrival time distribution (ATD) of these ions is measured at a detector after they exit the cell. Different peaks in the ATD for each cluster size correspond to different structural isomers.
linear forms takes place at a smaller cluster size for the cations than for the neutral and anionic clusters. For the cations, this transition appears to occur at C$_7^+$, compared to C$_{10}^+$ for the neutrals$^{67,68}$ and somewhere between C$_{10}^+$ and C$_{12}^+$ for the anions.$^{227}$

The ion mobility results obtained for C$_7^+$ can be generalized to explain the isomeric distributions of other carbon clusters that possess low-energy linear and cyclic forms. Despite the apparently large energy difference between the C$_7^+$ ring and chain isomers, linear chains are still experimentally observed. This is also the case for C$_6$, C$_{10}$, and larger clusters that possess cyclic ground states. At the high temperatures under which carbon clusters typically form, entropy favors the linear isomer even when the ring is significantly more stable. Because of the high barriers that exist between rings and chains, there is often no chance for the clusters to anneal to their most stable forms, so that the metastable linear isomers are “frozen out.” This may partly explain the scarcity of experimental data for the cyclic isomers of neutral carbon clusters.

### XI. C$_8$

#### A. Theory

C$_8$ is analogous to C$_4$ and C$_6$ in that both a cyclic structure and a $C_2v$ linear chain are believed to be low-energy isomeric forms. The early SCF calculations of Raghavachari and Binkley predicted that a planar monocyclic ring of C$_8$ symmetry was the ground-state structure (see Figure 1).$^{67}$ The linear structure was studied by Martin et al. at the UHP/6-31G* level as part of their study of structures and harmonic frequencies of C$_6$–C$_9$.$^{244}$ These authors argued that the assignment of the 1998 cm$^{-1}$ matrix absorption to linear C$_8$ was in error,$^{234}$ upon the basis of their frequency predictions and from the annealing behavior of this band. They suggested that this band was more likely due to C$_9$ while the most intense C$_8$ absorption probably occurred at higher frequency. One of the unresolved transitions near 2075 cm$^{-1}$ was suggested as the most likely candidate for C$_8$. The linear structure was also studied at the MP2/6-31G* level by Kurtz and Adamowicz.$^{218}$ More recently, Schmatz and Botschwina used large-scale open-shell coupled cluster methods with 272 cGTO’s to study geometries and symmetric vibrational frequencies for two electronic states of linear C$_8$ and the ground state of linear C$_8$.$^{76}$ Equilibrium bond lengths of C$_8$, obtained at the RCCSD(T) level (after a standard 0.007 Å correction), were 1.2969, 1.2879, 1.2726, and 1.2788 Å for the outer to inner bonds.

The nature of the cyclic minimum has recently been the subject of some controversy. As stated above, Raghavachari and Binkley found a planar monocyclic ring structure of C$_{8h}$ symmetry to be the minimum at the SCF/6-31G* level.$^{67}$ However, using an MP2/6-31G* technique, Slanina et al. located a nonplanar ring of D$_{2h}$ symmetry, possessing a boat-like conformation, 13 kcal/mol lower in energy than the C$_{8h}$ planar ring.$^{251,262}$ In this study, the planar structure was actually a saddle point on the potential surface. Upon the basis of previous experience with
the C₈ cluster, however, these results should be viewed with some skepticism. Recall that for C₆, it was found that only techniques which take electron correlation into account at high order produce reliable predictions of the relative energies.²²,²³ Martin and Taylor investigated these structures at the CCSD(T)/6-31G* level.₃⁸ Their findings indicated that the planar monocyclic ring of C₆₈ symmetry is indeed a minimum on the potential surface (see Figure 1). The nonplanar D₂₈ structure was found to lie 4.1 kcal/mol above the planar minimum. At this level of theory, the linear isomer was predicted to be the global minimum, lying 11.3 kcal/mol below the cyclic isomer. By expanding the basis set to cc-pVTZ quality, the linear—cyclic energy splitting was reversed, such that the cyclic form became the global minimum by 10.1 kcal/mol. In any case, as Martin and Taylor pointed out, relative energy calculations performed at the MP2 level on clusters of this size produce numerous artifacts and should be viewed with caution.

B. Experiment

1. The Cyclic Isomer

Wang et al. have recently reported the detection of cyclic C₈ trapped in an Ar matrix at 10 K.⁴⁵ These authors assigned an infrared absorption transition at 1844.2 cm⁻¹ to the ν₁(υ₅) fundamental transition of cyclic C₈. This assignment was made based upon agreement between the frequency and isotopomer frequency shifts and the results of density functional theory calculations.

2. The Linear Isomer

The linear triplet form of C₈ was first detected via its ESR spectrum in a solid Ar matrix.²²³ Szczepanowski et al. recently made tentative assignments of two infrared Ar matrix absorptions as being due to the ν₆ (2071.5 cm⁻¹) and ν₅ (1710.5 cm⁻¹) antisymmetric stretch bands of linear C₈.¹¹¹ These assignments were based on similarities in the annealing behavior of the two bands and agreement with the density functional theory calculations of Hutter et al.⁶⁰ These same bands were observed from mass-selected C₈ deposited in a Ne matrix at 2067.8 and 1707.4 cm⁻¹,²²⁸,²⁶³ which further supports the assignment of these transitions to ν₆ and ν₅, respectively.

C₈ is the only carbon cluster in the C₂–C₈ size range for which the linear isomer has not been characterized by high-resolution spectroscopy. Infrared diode laser searches in the regions of 1690–1720 and 2050–2100 cm⁻¹ yielded no spectra that could be attributed to linear C₈. It would appear that the number density of linear C₈ molecules produced in the laser vaporization source is below the detection limit of the diode laser spectrometer. Previous experiments on C₄²⁰² and C₆²³⁶ have shown that the even-numbered triplets are produced in less abundance than the odd singlets. In addition, the infrared intensities of the triplet bands are predicted to be significantly smaller than those of the singlets.⁶² These factors may have thus far precluded detection of the antisymmetric stretch bands of C₈.

Very little information on C₈ was obtained from the negative ion photoelectron spectra observed by Arnold et al., due to its high electron affinity.⁴¹ Only two peaks were resolved with a separation of 565 cm⁻¹. This separation was tentatively assigned as the ν₄ symmetric stretch, although assignment to a low-lying electronic state could not be ruled out. A much more complete picture of C₈ has emerged from recent photoelectron spectroscopy experiments by Xu et al.⁴² In particular, the band previously assigned to ν₄ was reassigned as the origin of the ¹Δ₉ electronic spectrum. In addition, two peaks lying 1928 and 1361 cm⁻¹ from the origin were observed and found to be consistent with the ν₁ and ν₃ symmetric stretch fundamentals.

C. Excited Electronic States

Liang and Schaefer calculated term energies for the ¹Δ₉ and the ¹(Σₙ) states of linear C₈ to be 0.141 and 0.010 eV, respectively.¹⁸⁶ The calculation was performed at the CISD/DZP level using Davidson’s correction. Xu et al. recently measured the term energy of the ¹Δ₉ state to be 0.071 ± 0.015 eV (605 cm⁻¹) using photoelectron spectroscopy of C₈.⁴² These authors also observed the ¹Σ⁺, the ¹Σ⁻, and (tentatively) the ¹Π from states with term energies of 0.115 ± 0.015 (927 cm⁻¹), 0.78 ± 0.02, and 1.03 ± 0.02 eV, respectively. ³Σ⁺–X³Σ⁻ vibronic transitions, with a band origin of 15630 cm⁻¹, were observed by Freivogel et al. for mass-selected C₈ using the same electronic spectroscopy technique that was applied to C₄ and C₆ (see Figure 1).⁷⁰⁷

D. C₈⁻

The C₈⁻ anion is linear with a ²Π₂ ground electronic state.⁷⁶,¹⁷⁶ The ground-state equilibrium geometry was calculated at the RCCSD(T)/272 cGTO level by Schmatz and Botschwina.⁷⁶ An equilibrium rotational constant of 0.0202 cm⁻¹ was derived from the calculated bond lengths. As was also the case for C₆⁻ and C₇⁻, there was no evidence for a cyclic isomer of C₈⁻ in the ion mobility experiments.²²⁷,²³⁹ Freivogel et al. observed a transition at 1796.0 cm⁻¹ from mass-selected C₈⁻ deposited in a Ne matrix that they assigned as the ν₆ antisymmetric stretch.²²⁸ The C²Π₂−X²Π₀ electronic spectrum has been measured for C₈⁻ trapped in a Ne matrix, with a band origin of 12 933 cm⁻¹,²⁰⁷ and in the gas phase by resonant two-photon photodetachment at 12 963 cm⁻¹.⁴⁸ More recently, Freivogel et al. measured the 2Σ⁺−X²Π₀ and the (2)Π₀−X²Π₀ bands of mass-selected C₈⁻ in a Ne matrix.²¹³ The band origins were 9545 and 16 295 cm⁻¹, respectively.

E. C₈⁺

Ion mobility experiments have shown that C₈⁺ exists in two isomeric forms—a planar monocylic ring and a linear chain.²⁴¹–²⁴³ Annealing studies similar to those described for C₇⁺ revealed that C₈⁺ possesses a cyclic ground-state geometry.²⁴¹ von Helden et al. used a simple kinetic model to estimate the energy difference between the cyclic and linear
isomers to be 23 ± 8 kcal/mol. The ground-state structure of the cyclic isomer was predicted to be a C_9 planar monocyclic ring with a “A” electronic state at the ROHF/6-31G(d) level of theory. The ground electronic state of the linear isomer was 4Σ_orb at this same level.

XII. C_9

A. Theory

C_9 is the largest neutral carbon cluster for which the ground-state structure is predicted to be a linear chain. The properties of the 13Σ_orb ground electronic state have been calculated at numerous levels of theory. Martin et al. calculated harmonic vibrational frequencies and intensities at the HF/6-31G* level. As has already been discussed, their calculations led to a reassignment of the matrix absorption at 1998 cm\(^{-1}\) to the \(v_6\) antisymmetric stretch of C_9. The assignment was based on harmonic frequency predictions and upon observed annealing behavior. The authors reasoned that the strong annealing behavior observed for the 1998 cm\(^{-1}\) band was most consistent with stepwise condensation of C_3 in the matrix. Kurtz and Adamowicz calculated minimum energy structures and vibrational spectra at the MBPT(2)/6-31G\(^*\) level. For C_9 they found that the equilibrium geometry was slightly bent from the linear configuration, with angles between adjacent bonds of 177°–179°. Although these bending angles were most likely due to artifacts, the authors claimed that the harmonic frequencies calculated at this level were still valid.

Martin and Taylor have performed more recent calculations at the CASSCF and the CCSD(T)\(^{26}\) levels of theory using the cc-pVDZ basis set. Again the main focus of these calculations was to study the vibrational spectrum. The authors noted that, for linear carbon clusters, as the size of the chain increases, such treatments as HF, SCF, and MP2 become less reliable, producing results that deviate more strongly from experiment. This is due to nondynamical correlation effects, which for smaller systems, are effectively dealt with using coupled cluster techniques. However, for systems larger than C_9, the coupled cluster methods are prohibitively costly at present. Therefore, the authors used C_9 to test the utility of CASSCF calculations for larger linear chains. They obtained reliable results for the harmonic frequencies of C_9, although relative intensities at this level were not predicted correctly. The CCSD(T)/cc-pVDZ study of Martin and Taylor are the largest scale calculations to be performed on C_9 to date. The authors used these calculations to predict bond lengths and harmonic stretching frequencies. They noted that bond lengths calculated at this level are consistently too long by as much as 0.01 to 0.02 Å, although harmonic frequencies are the most accurate that can be obtained for a system this large.

In addition to the very intense \(v_6\) band, the \(v_5\) and \(v_7\) bands were also predicted to have appreciable infrared intensities. By scaling the calculated harmonic frequencies for C_3–C_9 with known experimental values, the authors predicted the \(v_5\) band to occur at 2101 ± 14 cm\(^{-1}\) and the \(v_7\) band at 1607 ± 12 cm\(^{-1}\). Recent experimental measurements of these two bands are in satisfactory agreement with these predictions and will be discussed below.

Slanina et al. recently investigated the possibility of a cyclic isomer for C_9. They obtained a C_9 nonplanar structure, lying just 6 kcal/mol above the linear ground state, at the MP2/6-31G* level. However, more recent calculations by Martin et al. showed the cyclic structure to be a planar monocyclic ring of C_2\(^v\) symmetry, for which the relative energy was 9 kcal/mol above the chain. Once again, the MP2 results were shown to be artifactual. Finally, Wu et al. calculated the cyclic–linear energy spacings of C_9 using HF, MP2, and DFT techniques, in connection with their theoretical study of the LaC_9\(^{+}\) ion.

B. Experiment

After reassignment of the 1998 cm\(^{-1}\) matrix absorption to the \(v_6\) vibration of C_9 by Martin et al., Heath and Saykally discovered this band in the gas phase using diode laser spectroscopy of a supersonic cluster beam. Rovibrational transitions were measured with J values as large as J = 80. In a later diode laser spectroscopy study by Van Orden et al., the \(v_6\) fundamental transitions were remeasured after improvements in the sensitivity of the spectrometer. Due to the improved signal-to-noise ratio, the lowest energy rovibrational transitions, P(2) and R(0), were observed, which facilitated an unambiguous rotational assignment. It was found that the original assignment by Heath and Saykally was in error by two units in J. In addition, the precision of the frequency positions was improved by more than a factor of 4, from 0.0035 to 0.0008 cm\(^{-1}\). Thus, some of the anomalous behavior reported by Heath and Saykally, including perturbations of the low-J transitions and large, negative values for the centrifugal distortion constants, were determined to be artifacts of the lower precision measurements and the incorrect rotational assignment. The gas-phase frequency of \(v_6\) was measured as 2014.277 ± 0.008 cm\(^{-1}\), which represents a 16 cm\(^{-1}\) red-shift of the same band in the Ar matrix.

In addition to the improvements in the analysis of the \(v_6\) fundamental transitions, Van Orden et al. also observed hot band transitions arising from the lowest frequency \(v_{15}\) bending mode. The \((v_6 + v_{15}) - 2v_{15}\) band with J values up to 57 and the \((v_6 + 2v_{15}) - 2v_{15}\) band with J up to 34 were observed in the region of the antisymmetric stretch. The signal-to-noise ratio of the \((v_6 + v_{15}) - v_{15}\) transitions were about 10 times less than the fundamental peaks. Experimental hot band and fundamental transitions are shown in Figure 21. Molecular parameters obtained from the analysis of these bands are shown in Table 11. There was no evidence for large amplitude motion in the bending coordinate from these data, although there was evidence for Coriolis-type perturbations to the symmetry components of the \((v_6 + v_{15}) - v_{15}\) band due to large centrifugal distortion constants. Excitation of the bending vibrations resulted in an increase in the rotational constant that is characteristic of a
Table 11. Molecular Parameters of X1Σ−/C9

<table>
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<th>parameter</th>
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<th>theory</th>
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a Numbers in parentheses are uncertainties in the last digits. Numbers in brackets are calculated infrared intensities [km/mol]. b Infrared diode laser spectroscopy. c B3LYP/cc-pVDZ. d CCSD(T)/cc-pVDZ. e Anion photoelectron spectroscopy. f CCSD/6-31G*. g Ar matrix. h Ar matrix. i Infrared diode laser spectroscopy.

= 1 state and the small redshift in the (νı6 + νı15) – νı15 band origin also characterized the molecule as a fairly well-behaved semirigid linear chain.

Recently, the two other infrared active stretching frequencies were observed experimentally. Kranze et al. confirmed that an Ar matrix absorption at 1601.0 cm−1 corresponds to the ν7 band of C9. These authors used extensive isotopic substitution experiments along with density functional theory calculations to predict isotope shifts, confirming the carrier of the band. Van Orden et al. observed the gas-phase rovibrational spectrum of the ν5 band at 2079.6736(2) cm−1. A diode laser spectrometer was used to observe 28 rovibrational transitions with J values up to 42. Table 11 displays molecular constants obtained from a simultaneous fit of the ν5 and νı6 spectra. By comparing the absorbance of ν5 and νı6 transitions, the authors measured the relative IR intensity of ν5 to be 0.11 ± 0.01 compared to νı6. Large disparities were found between this measured value and the relative IR intensities calculated at various levels of theory, underscoring the difficulty encountered when calculating IR intensities for a molecule of this size.

More recently, matrix absorptions at 2081.1 cm−1 (Ne) and 2078 cm−1 (Ar) were assigned to the ν5 vibration of C9 by Maier and co-workers and Szczepanski et al., respectively. The latter authors also assigned the νı4 + ν5 combination band (2525.7 cm−1) and the 2ν5 (3996.5 cm−1) and 2νı5 (4156.2 cm−1) overtone bands. On the basis of the latter two results, anharmonicity constants of ν5 = 0.0 cm−1 and νı5 = 0.25 cm−1 were obtained. Finally, two of the symmetric stretch frequencies of C9 were measured by Arnold et al. using anion photoelectron spectroscopy. The νı3 mode was found to occur at 1258 ± 50 cm−1 and the νı4 mode was measured at 484 ± 48 cm−1.

Figure 21. Rovibrational spectra and a simulated stick spectrum of the νı6 fundamental (strong peaks) and (νı6 + νı15) – νı15 hot band of linear C9 near 2014 cm−1 at 30 K. Subscripts on the P- and R-branch labels indicate the bending excitation level of the lower state. Asterisks mark unassigned peaks. (Modified from ref 269.)
C. Excited Electronic States

By extrapolating the term energies calculated for odd-numbered C3–C9, Kolbuszewski predicted the $^1\Sigma_u^+$ state of C9 to lie at 5.16 eV.225 This corresponds to a $^1\Sigma_u^+\rightarrow X^1\Sigma_u^+$ transition wavelength of 240.3 nm. Kurtz and Huffman observed a strong correlation in the annealing behavior between the IR Ar matrix absorption at 1998 cm$^{-1}$,204 which was later assigned to C9, and a UV band at about 310 nm. This same correlation was observed by Szczepanski and Vala.205 Assignment of this transition to C9 was recently confirmed by Forney et al.214 These authors measured the band origin of the $^1\Sigma_u^+\rightarrow X^1\Sigma_u^+$ band of mass-selected C9 in a Ne matrix to be 33 895 cm$^{-1}$ (295.0 nm).

D. $^{1}\text{C}_{9}^{-}$

C9$^-$ is a linear chain with a $^3\Pi_u$ ground electronic state.176 The arrival time distribution (ATD) measured after mass-selected C9$^-$ clusters passed through a He drift tube is shown in Figure 22.241 The ATDs of C12$^-$, C26$^-$, and C36$^-$ are also shown for comparison and will be discussed later. The ATD of C9$^-$ is dominated by a peak corresponding to the linear isomer, although a weak shoulder appearing at shorter time is due to the monocyclic ring. Other experimental techniques that have been used to study C9$^-$ are anion photoelectron spectroscopy,41 resonance-enhanced multiphoton electron detachment (REMPED),49 and infrared217,228 and electronic214 absorption spectroscopy of C9$^-$ trapped in rare gas matrices.

Figure 22. Arrival time distributions (ATDs) for C9$^-$, C12$^-$, C26$, and C36$^-$ measured using gas-phase ion chromatography. The large peak in the ATD of C9$^-$ is due to the linear isomer. For C12$^-$, the peak at shorter time is due to the monocyclic ring and the peak at longer time to the linear chain. For C26$^-$, the two peaks are due to the monocyclic ring at longer time and the bicyclic ring at shorter time. Five isomers are present for C36$. The broad feature at longer time is due to monocyclic, bicyclic, and tricyclic rings. The peak at shorter time is the graphitic isomer, and the peak shown on the expanded scale is the fullerene isomer. (Reprinted with permission from ref 227. Copyright 1995 Elsevier Science B.V.)

E. $^{1}\text{C}_{9}^{+}$

Both linear and monocyclic ring isomers were observed for C9$^+$ in the gas-phase ion chromatography experiments of von Helden et al., as was also the case for C7$^+$ and C8$^+$.241–243 Annealing studies showed that the cyclic isomer was more stable than the linear chain by 17 ± 8 kcal/mol.241 The cyclic ground state was found to be a planar monocyclic C2 structure at the ROHF/6-31G(d) level of theory.241 A $^2\Sigma^+$ state was found to be the ground electronic state of the linear isomer using this same technique.

XIII. C10

A. Theory

The C10 molecule has long been recognized as a geometric transition point for small neutral clusters, which generally prefer linear geometries, and larger clusters, which are believed to form planar monocyclic ring structures, due to reduced angle strain for larger rings.67 The cyclic C10 cluster is also of interest because it satisfies Huckel’s rules for aromaticity, which may impart added stability to the ring. Experimental evidence for the unusual stability of cyclic C10 was provided very recently by Wakabayashi et al.270 These authors used tandem IR and UV pulsed laser irradiation of graphite to produce molecular beams of carbon cluster anions, which were then detected using time-of-flight mass spectrometry. Under conditions in which the separation between the IR and UV pulses was between 50 and 200 μs, it was found that C10$^-$ ions were formed almost exclusively. The authors took this result as evidence for preferential formation of neutral C10, presumed to be cyclic, under these conditions, since the anions were thought to form as products of the reaction between neutral clusters and photoelectrons in the cluster source.

In the SCF calculations of Raghavachari and Binkley, a cyclic structure of D9h symmetry was determined to be the ground state of C10.67 Liang and Schaefer performed calculations at the CISD/DZP level to study the relative isomer energies of the cumulenic and acetylenic triplet states of the linear chains as well as three monocyclic rings.68 The ring structures investigated were a cumulenic D10h structure, a D9h isomer, in which cumulenic double bonding occurs, and a D9h isomer with acetylenic bonding.
These structures are labeled as 1, 2, and 3, respectively, in Figure 23. At the highest level of theory considered (CISD/DZP including Davidson's correction), the cumulenic $D_{5h}$ ring was found to be the global minimum, lying 67 kcal/mol below the lowest energy linear structure. The relative energies of the linear structures depended strongly upon the level of theory and the basis set. Liang and Schafer investigated these effects by performing calculations at the SCF and CISD levels using both the DZP and the 3-21G basis sets. The acetylenic structure of linear C$_{10}$ was actually the lowest energy form for the lower levels of theory. Only after the Davidson correction was applied at the CISD/DZP level did the cumulenic structure emerge as the most stable linear chain by 4.9 kcal/mol. Similar effects were observed in the relative energy calculations of the monocyclic rings. At the CISD/3-21G level, the acetylenic $D_{5h}$ structure was lowest in energy, while calculations at the CISD/DZP level with the Davidson correction found this structure to be least stable. Electron correlation effects had a strong influence on the energy spacing between the $D_{5h}$ and the $D_{10h}$ cumulenic isomers. While the $D_{5h}$ structure was lower in energy, increasing the level of electron correlation systematically reduced the relative energy. Thus, the authors could not confirm that the $D_{5h}$ structure would still be the global minimum at higher levels of theory.

Watts and Bartlett studied the structures and energetics of cyclic C$_{10}$ isomers at higher levels of electron correlation using coupled cluster methods. The $D_{5h}$, cumulene, the $D_{5h}$ acetylene, and the $D_{10h}$ cumulene were again investigated, this time at the CCSD+T(CISD) and the CCSD(T) levels, using the cc-pVDZ basis set. They also reported SCF and second-, third-, and fourth-order MBPT results for comparison, although these methods were generally found to be artifactual for studying a system of this size. The DZP and 4s3p1d basis sets were used to study basis set effects on the relative energies. At the CCSD(T)/cc-pVDZ level of theory, the $D_{5h}$ cumulene was the lowest energy isomer, lying 2.4 kcal/mol lower in energy than the $D_{10h}$ structure. However, when the basis set was expanded to 4s3p1d quality, the CCSD(T) level of theory predicted an energy separation that was reduced to within the expected errors of the calculation. A vibrational analysis of the three structures indicated that the $D_{5h}$ structure was a local minimum. The $D_{10h}$ structure was most likely a transition state along a ring deformation coordinate of the $D_{5h}$ structure, in which the vibrational motion interconverts the molecule between two equivalent minima. Force constant calculations indicated that this vibration of the $D_{5h}$ isomer was very floppy. Because of the large zero point energy of cyclic C$_{10}$, it is most likely that the effective vibrationally averaged structure that would be observed experimentally would be the $D_{10h}$ ring.

Martin and Taylor investigated the relative energies of the $D_{5h}$ and $D_{10h}$ cumulenes as part of their coupled cluster study of the vibrational spectrum of small carbon clusters. They confirmed that the $D_{10h}$ structure is a transition state at the CCSD(T)/cc-pVTZ level, lying an estimated 1.0 ± 0.1 kcal/mol above the $D_{5h}$ minimum. Again it was predicted that the vibrationally averaged structure would possess $D_{10h}$ symmetry. The harmonic frequencies of the three vibrationally active e$_1''$ modes were calculated at the CCSD(T)/cc-pVDZ level of theory. The most intense transition was predicted to occur at 2011 cm$^{-1}$, which the authors speculated may correspond to a matrix absorption at 1915 cm$^{-1}$. This peak grows very strongly with annealing as would be expected for a cyclic carbon cluster.

**B. Experiment**

Despite the theoretical predictions that the most stable form of C$_{10}$ should be cyclic, the only experimental data that exist for the neutral cluster is for the linear isomer. This is also the case for C$_{11}$, C$_{13}$, and C$_{15}$, to be discussed below. It is interesting to note that, even for the extremely large linear—cyclic energy splitting that has been predicted for C$_{10}$, the linear chain still seems to be the favored isomer under experimental conditions. The ESR spectrum of C$_{10}$ was detected in solid Ar along with those of linear C$_4$, C$_6$, and C$_8$. The zero field splitting parameter, |D|, for C$_{10}$ was the lowest value observed for these clusters, which was anomalous since |D| increased with cluster size for C$_4$–C$_8$. It was suggested that this relatively low zero field splitting may be due to a nonlinear structure.

Freivogel et al. have recently reported observation of two infrared transitions at 2074.5 and 1915.4 cm$^{-1}$ that were present after a Ne matrix containing mass-selected C$_{10}^-$ was irradiated with UV light.
bands were tentatively assigned as antisymmetric stretches of linear C\textsubscript{10}, although assignment of one of these bands to the cyclic isomer cannot be ruled out, since theoretical calculations predict that an infrared active transition should occur in this region.\textsuperscript{62}

C. Excited Electronic States

Liang and Schaefer’s CISD/DZP predictions, including Davidson’s correction, for the low-lying singlet states of linear C\textsubscript{10} were 2.71 kcal/mol for the \( ^1\Sigma_g^+ \) state and \(-2.28 \) kcal/mol for the \( ^3\Sigma_g^+ \) state.\textsuperscript{186} The \( ^1\Sigma_g^+ \) state was actually found to be lower in energy than the \( ^3\Sigma_g^+ \) state, although the experimental ESR measurements support a \( ^3\Sigma_g^+ \) ground state. Freivogel et al. measured three vibronic transitions that were assigned to the \( ^3\Sigma_g^- \rightarrow ^3\Sigma_u^+ \) band of linear C\textsubscript{10} in a Ne matrix, whose origin occurred at 13 596 cm\textsuperscript{-1}.\textsuperscript{207} However, in more recent work this band was attributed to the \( ^2\Pi_g \rightarrow ^2\Pi_u \) spectrum of linear C\textsubscript{10}.\textsuperscript{213} A new band measured at 12 985 cm\textsuperscript{-1} has now been attributed to the \( ^3\Sigma_g^- \rightarrow ^3\Sigma_u^+ \) band origin of neutral C\textsubscript{10} (see Figure 13).\textsuperscript{213}

D. C\textsubscript{10}\textsuperscript{-}

C\textsubscript{10}\textsuperscript{-} is the smallest carbon cluster anion for which a significant fraction of the planar monocyclic ring isomer is observed in the ATD of the ion chromatography experiments.\textsuperscript{227,239} Both the linear and cyclic forms are present, and, depending upon experimental conditions, one isomer can be made to dominate over the other. Annealing experiments performed to determine the relative stabilities of the linear and cyclic anions were significantly more difficult to interpret than for the cations.\textsuperscript{227} This is due to the lower barriers that are thought to exist between the linear and cyclic minima of the anions. Increasing the energy at which the ions were injected into the He drift cell was found to favor the formation of linear isomers for cluster anions in the C\textsubscript{10}\textsuperscript{-}—C\textsubscript{15}\textsuperscript{-} size range. For example, the isomer distribution of C\textsubscript{10}\textsuperscript{-} was shifted to almost 100% linear at an injection energy of 100 eV. One possible explanation for this observation could be that the ground-state structures of these clusters are the linear chains. Alternatively, the formation of linear isomers at increased injection energies could be due to their higher density of states at these energies. Bowers and co-workers favor the latter explanation and consider the cyclic isomers to be the ground states for these clusters,\textsuperscript{227} although the energy differences between the two isomers are probably quite small (\( \pm 5 \) kcal/mol). Theoretical calculations that address these issues would be of great value.

C\textsubscript{10}\textsuperscript{-} has been studied experimentally by photoelectron (PE) spectroscopy,\textsuperscript{41L77,78,272,273} and infrared\textsuperscript{228} and electronic\textsuperscript{207,213} absorption spectroscopy of mass-selected C\textsubscript{10}\textsuperscript{-} deposited in a Ne matrix. Evidence for a linear to cyclic transition at C\textsubscript{10} was provided by the photoelectron spectroscopy experiments of Yang et al.\textsuperscript{77,78} and more recently, by the PE studies of Handschuh et al. on annealed cluster ions.\textsuperscript{273} Arnold et al. observed broad, unresolved features in their anion photoelectron spectra of C\textsubscript{10}\textsuperscript{-} that they attributed to transitions between nonlinear isomers of the anion and/or the neutral cluster.\textsuperscript{41} However, Achiba et al. reported evidence for both cyclic and linear isomers of C\textsubscript{10}—C\textsubscript{20} in their photoelectron spectra in which the clusters were formed under different experimental conditions.\textsuperscript{272} The disparity between these observations underscores the complex competition between linear and cyclic isomers observed by Bowers and co-workers.\textsuperscript{207,239}

Electronic absorption spectroscopy of mass-selected cluster ions deposited in Ne matrices has been used to measure the C\textsubscript{2}\Pi\textsubscript{g} \rightarrow \chi\Pi\textsubscript{u}, the (2)\Pi\textsubscript{g} \rightarrow \chi\Pi\textsubscript{u}, and the B\textsuperscript{3}Sigma\textsuperscript{-} \rightarrow \chi\Pi\textsubscript{u} bands of linear C\textsubscript{10}.\textsuperscript{207,213} The band origins were at 10 338, 13 596, and 8964 cm\textsuperscript{-1}, respectively. Freivogel et al. observed an infrared absorption at 2094.5 cm\textsuperscript{-1} in the Ne matrix that they attributed to an antisymmetric stretch vibration of linear C\textsubscript{10}\textsuperscript{-}.\textsuperscript{228}

E. C\textsubscript{10}\textsuperscript{+}

Ion chromatography experiments indicated that C\textsubscript{10}\textsuperscript{+} is formed overwhelmingly as a planar monocyclic ring.\textsuperscript{241—243} Only a very small fraction of the ions were present in the linear form. Annealing studies showed that the cyclic isomer was about 47 ± 8 kcal/mol more stable than the linear chain.\textsuperscript{241} An ROHF/6-31G(d) calculation predicted that the ground state was a C\textsubscript{2v} structure with a 2\textit{A}\textsuperscript{+} electronic state.\textsuperscript{241}

XIV. C\textsubscript{11} and Beyond

A. Theory

Clusters in the C\textsubscript{11} to C\textsubscript{20} size range are predicted to exist predominantly as monocyclic rings. At this size, the angle strain associated with closing the ring is small, while added stability arises from forming an additional carbon—carbon bond. Unfortunately, very high level ab initio techniques such as coupled cluster methods are currently too costly to be performed on clusters of this size. While perturbative methods such as MP2 have been performed for C\textsubscript{11},\textsuperscript{274} C\textsubscript{13},\textsuperscript{275} and larger systems\textsuperscript{276} to calculate structures and linear—cyclic energy spacings, we have already addressed the limitations of these techniques from results on the smaller clusters. The highest level calculations to be performed on clusters in this size range are the CASSCF studies applied to linear C\textsubscript{11} and C\textsubscript{13} by Martin et al.\textsuperscript{264} In general, theoretical calculations for clusters of this size must be viewed with caution, as we have seen the importance of treating electron correlation at high levels of theory, which is difficult to accomplish for these larger species.

Density functional theory (DFT) has recently emerged as a technique that can be applied to much larger systems than more accurate ab initio methods such as coupled cluster, due to its lower CPU time dependence on the size of the system. In general, DFT calculations of the structures and vibrational frequencies of smaller clusters are in excellent agreement with more sophisticated coupled cluster calculations and with experiment.\textsuperscript{60,62} However, the ac-
accuracy of these techniques has not been verified for systems larger than C\textsubscript{10}. Hutter et al. used the BLYP level of DFT to calculate structures, relative isomer energies, and vibrational frequencies for C\textsubscript{2n}\textsubscript{−15}.\textsuperscript{60} For the small C\textsubscript{2}−C\textsubscript{9} clusters, this technique reproduced structural parameters and harmonic frequencies that were generally in good agreement with coupled cluster calculations.\textsuperscript{59} The exceptions were that a bent equilibrium structure was obtained for C\textsubscript{3}, and a C\textsubscript{2n}\textsubscript{−} structure was found to be the lowest ring isomer of C\textsubscript{8}. For the relative isomer energies of C\textsubscript{4}, C\textsubscript{6}, and C\textsubscript{8}, the density functional treatment was found to overestimate the stability of the linear triplet states. Thus, quantitative agreement with the higher levels was not achieved, although in all cases the chain and the ring were close in energy. For the odd-numbered clusters in the C\textsubscript{11}−C\textsubscript{17} size range, the authors found that planar, monocyclic rings were lower in energy than the chains. However, imaginary vibrational frequencies were calculated for all these clusters, leading the authors to conclude that the true ground states should have three-dimensional structures. For the even-numbered C\textsubscript{12}−C\textsubscript{18} clusters, the planar monocyclic rings were also more stable than the chains. While C\textsubscript{12} and C\textsubscript{14} were both local minima, C\textsubscript{16} and C\textsubscript{18} had imaginary frequencies.

Martin et al. used the more sophisticated B3LYP level of DFT to study the even-numbered C\textsubscript{12}−C\textsubscript{18}.\textsuperscript{62} They also performed calculations on C\textsubscript{2}−C\textsubscript{10} for comparison with higher level results. Better structural agreement with the coupled cluster calculations was achieved in that the structures of C\textsubscript{3} and cyclic C\textsubscript{8} were predicted correctly. The vibrational frequencies of these smaller clusters were of the same level of accuracy for predicting experimental values as the CCSD(T)/cc-pVDZ predictions, although linear−cyclic energy spacings for the even clusters showed a bias toward the linear triplets when compared to higher level results. For the larger clusters, this study found that the planar monocyclic rings of C\textsubscript{12}−C\textsubscript{18} were all local minima, in contrast to the work of Hutter et al.\textsuperscript{60} Cyclic C\textsubscript{4n+2} clusters, including C\textsubscript{8} and C\textsubscript{10}, were predicted to be doubly aromatic, such that the valence electrons are delocalized in two perpendicular systems of π orbitals, one in the plane of the ring, and the other out of the plane.\textsuperscript{62} Martin et al. found that the most stable structures for these clusters were of D\textsubscript{2n+1-h} symmetry with cumulenic bonding configurations. In contrast, the cyclic C\textsubscript{4n} clusters, including C\textsubscript{8}, existed in planar rings of C\textsubscript{2n} symmetry. The acetylenic forms of these C\textsubscript{4n} rings were determined to be lower in energy than the cumulenic forms.

More recently, Martin et al. have used density functional theory methods to examine structural properties, infrared spectra, and linear−cyclic isomerism of the odd-numbered C\textsubscript{2n+1} clusters in the C\textsubscript{5}−C\textsubscript{15} size range.\textsuperscript{247} CCSD(T)/cc-pVDZ methods were also used to calculate the relative isomer energies for the smaller linear and cyclic C\textsubscript{5}−C\textsubscript{11} systems. Not surprisingly, these results found that the linear isomers were strongly favored for clusters smaller than C\textsubscript{10}, although the energy difference dropped sharply with increasing cluster size, from 60 kcal/mol for C\textsubscript{5}, 14 kcal/mol for C\textsubscript{7}, and 9 kcal/mol for C\textsubscript{9}, as already discussed. For C\textsubscript{13}, the ring structure was predicted to be more stable by 27 kcal/mol at this level. For C\textsubscript{15}, the B3PW91 level of density functional theory was considered to be the best substitute for coupled cluster methods in the calculation of relative isomer energies. At this level, the monocyclic ring isomer was predicted to be more stable than the linear chain by 28 kcal/mol. Thus, according to the latest density functional theory results, linear isomers of clusters larger than C\textsubscript{11} are not expected to be energetically competitive with planar monocyclic rings. Despite these predictions, linear chains continue to be experimentally observed for clusters in this size range.

For clusters larger than ~C\textsubscript{20}, numerous low-energy structural isomers have been predicted to exist. These include linear chains, monocyclic and polycyclic rings, closed-cage fullerenes, graphitic sheets, and bowl-shaped isomers to be discussed below. Many of these isomers have been observed for carbon cluster ions larger than ~C\textsubscript{30} in the gas-phase ion chromatography experiments of Bowers and co-workers.\textsuperscript{227,242,243,277} Examples of the kinds of structures that have been observed are shown in Figure 24, which depicts several isomers of C\textsubscript{36}, deduced from ion chromatography experiments.\textsuperscript{227} DFT calculations have been used to study the isomers of C\textsubscript{20},\textsuperscript{259,278} C\textsubscript{24},\textsuperscript{261} and C\textsubscript{28}.\textsuperscript{264} In particular, these calculations predict that fullerene, graphitic, and bowl-shaped structures are the lowest energy isomers of these clusters, although the ion chromatography experiments have found no evidence for fullerene or graphitic structures for cluster ions this small, and no evidence for bowl-shaped isomers of any size.\textsuperscript{227,242,243,277} These issues will be discussed in more detail below with respect to the C\textsubscript{20} cluster. More recently, Jones and Seifert have used local spin density and gradient corrected DFT to study the isomers of C\textsubscript{14}−C\textsubscript{24}.\textsuperscript{265} For all clusters in this size range, the authors found numerous stable isomers, including linear chains, planar monocyclic and polycyclic rings, graphitic fragments, and closed-cage fullerene-like isomers. Again, there is no experimental verification for any structures besides linear chains and planar rings in this size range.

### B. C\textsubscript{20}

An interesting question regarding clusters in the C\textsubscript{15} to ~C\textsubscript{30} size range is, at what size does the closed cage fullerene-like structure begin to emerge as a stable isomer? This has been a difficult question to answer definitively because of the experimental and theoretical challenges posed by systems of this size. While it is fairly well established that, for even-numbered clusters above C\textsubscript{22}, fullerenes are the most stable isomers, it is not certain precisely where the transition from ring structures to fullerenes occurs. The ion mobility experiments by Bowers and co-workers revealed more than one isomer to be present for cluster ions larger than C\textsubscript{20}, with structures ranging from chains to polycyclic rings, although there was no evidence for fullerene structures smaller than C\textsubscript{30}.\textsuperscript{227,242,243,277} However, as alluded to above, several theoretical studies have shown that fullerene-
like closed-cage isomers may be low in energy for clusters as small as C$_{20}$ or smaller.$^{59,61,63,65,276,278-282}$ C$_{20}$ has received a lot of attention with regard to its possible role as the smallest fullerene.$^{279}$ Ion mobility experiments have indicated that C$_{20}$ cations produced by laser vaporization of graphite exist exclusively as monocyclic rings.$^{242,243,277}$ For the anions, a small quantity of linear chains and polycyclic rings also coexisted with the predominant monocyclic isomer.$^{227,239,277}$ There was no evidence for a fullerene isomer or a bowl-shaped structure. Three structural isomers have been considered as low-energy forms of C$_{20}$—a planar monocyclic ring, a curved graphitic bowl, and a closed-cage fullerene in the theoretical calculations. These isomers are diagramed in Figure 25. Brabec et al. used the local density approximation to study the annealing behavior of C$_{20}$ at various temperatures.$^{278}$ As the annealing temperature increased, the favored structures changed from the fullerene to a bowl-shaped corannulene-like structure to the monocyclic ring. Parasuk and Almlöf studied the relative energies of three planar monocyclic ring isomers and the fullerene with SCF and MP2 ab initio methods.$^{279}$ At the SCF level, an acetylenic D$_{10h}$ ring was predicted to be the ground state, with the fullerene lying over 100 kcal/mol higher in energy. However, inclusion of electron correlation at the MP2 level resulted in a reversal of the relative energies, with the fullerene lying over 60 kcal/mol lower in energy than the nearest ring. Raghavachari et al. used the BLYP level of density functional theory to study the monocyclic ring, the fullerene cage and the corannulene structures.$^{59}$ The BLYP level includes a gradient correction in the density functional treatment that was found to have a major effect on the relative energies. Without the gradient correction, the cage isomer was significantly lower in energy than the ring and the corannulene

Figure 24. Structural isomers of C$_{36}$ observed in gas-phase ion chromatography experiments. The structures were deduced from semiempirical quantum chemistry methods and theoretical modeling of the observed arrival time distributions. Different isomers of the bi- and tricyclic rings could not be ruled out from the data. (Reprinted with permission from ref 227. Copyright 1995 Elsevier Science B.V.)

Figure 25. Fullerene, corannulene-like bowl, and monocyclic ring isomers of C$_{20}$. (Reprinted with permission from ref 281. Copyright 1995 Elsevier Science B.V.)
forms. However, inclusion of the gradient correction yielded the monocyclic ring as the ground state by 3.44 eV over the fullerene.

More recent theoretical studies have predicted the bowl-shaped isomer to be the ground state of C_{20}, with the fullerene structure lying dose in energy and the ring at substantially higher energies. Grossman et al. used quantum Monte Carlo methods to predict the relative energies of a monocyclic ring, a corannulene-like bowl, and a cage structure at high levels of electron correlation. The structures investigated were those that had been optimized at the HF level. This work emphasized the importance of accurately treating electron correlation, finding that the more compact cage and bowl structures emerged as the lowest energy forms at this level of accuracy. Martin et al. used the B3LYP level of DFT to optimize the ring, bowl, and cage structures and to calculate relative energies and vibrational frequencies. The most stable ring isomer was a polyacetylenic C_{10h} structure which was estimated to lie 48.1 kcal/mol above the bowl and 38.4 kcal/mol above the cage. Taylor et al. used CCSD(T) calculations to study the three C_{20} isomers, making this the largest carbon cluster, and the only cluster larger than C_{11}, for which coupled cluster techniques at this level have been applied. The calculations were limited to ring, bowl, and cage structures that were fixed to SCF-optimized geometries. The structures considered are shown in Figure 25. The modest sized cc-pVDZ basis set was the smallest that could be used without sacrificing meaningful results. Even with these limitations, the calculation approached the limit of what can be achieved with modern supercomputers, making geometry optimization and exploration of basis set effects out of the question at this level. The energy calculations found that the bowl-shaped and cage isomers were nearly isoenergetic, with the ring lying 39 kcal/mol higher in energy.

It is interesting to note that the bowl-shaped isomer predicted to be the ground state of C_{20} is the smallest of the so-called "pentagon road" structures. These types of structures have been predicted to be low-energy isomeric forms for a number of larger carbon clusters as well. The "pentagon road" mechanism is a hypothesis for fullerene formation which states that the precursors to fullerene formation are highly reactive curve-shaped open cages with the carbon atoms arranged in pentagons and hexagons. "Pentagon road" structures are those that contain the maximum number of pentagons that can be arranged in such a way so that each pentagon is surrounded on all sides by five hexagons. Fullerenes formation is thought to occur when conditions are such that the smaller precursors have sufficient time to anneal to their most favorable "pentagon road" structures. Growth of these structures then proceeds to C_{60}, which is the smallest cluster for which the "pentagon road" structure is a closed cage, and to larger closed-cage fullerenes such as C_{70}, C_{84}, and so on.

Despite its elegance, the "pentagon road" mechanism is difficult to rationalize in light of recent experimental ion mobility studies by Bowers and co-workers andJarrold and co-workers. First, there are no isomers detected at any size, for which the ion mobility is consistent with these curved graphitic bowl or cup-like structures, although a recent attempt was made to produce such species from polychlorinated precursors. It was clearly shown that growth of these ions proceeds through linear chains to planar rings. Closed cages appear at C_{30} and become the dominant isomers above C_{40}, at least for the cations. Second, annealing studies of the cluster ions have shown that collisional heating of metastable cyclic isomers, followed by ejection of a small carbon fragment, is an efficient pathway to fullerene formation. For example, the ion mobility of C_{39} through the He drift cell showed that this cluster exists in several different cyclic forms. Most of these isomers were metastable, however, and were produced when the high-energy laser vaporization plasma was rapidly cooled in a supersonics expansion. Annealing of the clusters took place when the ions were injected into the drift cell at 150 eV. The main products of this annealing process were the monocyclic ring isomer of C_{39} and the fullerene isomers of C_{38} and C_{36}, which were accompanied by the ejection of C and C_{3} fragments, respectively. Thus, a more likely mechanism is that fullerenes are formed in laser vaporization or arc discharge sources through the growth of high-energy metastable cyclic clusters that subsequently anneal to fullerenes by evaporation of smaller fragments. Further evidence for fullerene formation from the coalescence of cyclic rings was provided by Rubin et al. and McElvany et al. These authors showed that fullerenes could be produced by laser desorption of such cycocarbon species as C_{10h}(CO)_{6}, C_{24}(CO)_{8}, and C_{30}(CO)_{10}. Hunter et al. have recently proposed a detailed mechanism for the formation of fullerenes from cyclic precursors.

C. Experimental Observations

1. Gas-Phase Infrared Spectroscopy of the Linear C_{13} Cluster

Most of the experimental information concerning C_{11} and larger carbon clusters has been provided by the gas-phase ion chromatography studies of carbon cluster ions to be discussed below. For the neutral species, experimental data are extremely sparse. Despite theoretical results predicting cyclic ground states for these clusters, only linear isomers have been detected experimentally. Even for clusters as large as C_{20}, the linear isomers are still competitive under experimental conditions, due to their much higher density of states, and consequently, their more favorable entropy of formation. The only definitive spectroscopic information for a cluster of this size is for linear C_{13}. This molecule is the only carbon cluster larger than C_{9} for which a rotationally resolved spectrum has been recorded. Giesen et al. measured 76 rovibrational absorption transitions in the frequency region between 1808.1 and 1809.7 cm^{-1} using infrared diode laser spectroscopy of a supersonic cluster beam. Figure 26 displays part of the observed spectrum. Transitions with J values up to
Table 12. Molecular Parameters of an Antisymmetric Stretch of $X^{1\Sigma_g^+}$C$_{13}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experiment</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_0$ (cm$^{-1}$)</td>
<td>1808.96399(7)$^b$</td>
<td>1.2668 1.2867 1.2581 1.2741 1.2537 1.2688$^c$</td>
</tr>
<tr>
<td>B$^a$ (cm$^{-1}$)</td>
<td>0.0047324(6)$^b$</td>
<td>1.2717 1.2914 1.2623 1.2786 1.2679 1.2731$^d$</td>
</tr>
<tr>
<td>B$^c$ (cm$^{-1}$)</td>
<td>0.0047218(6)$^b$</td>
<td>1.2668 1.2867 1.2581 1.2741 1.2537 1.2688$^c$</td>
</tr>
<tr>
<td>$r_0$ (Å)</td>
<td>1.2770(5)$^b$</td>
<td>1.2668 1.2867 1.2581 1.2741 1.2537 1.2688$^c$</td>
</tr>
</tbody>
</table>

$^a$ Numbers in parentheses are uncertainties in the last digits. $^b$ Infrared diode laser spectroscopy. $^c$ Outer to inner equilibrium bond lengths, calculated at the MP2/6-31G$^*$ level. $^d$ Same as $c$ at the B3LYP/cc-pVDZ level.

Figure 26. The infrared rovibrational spectrum of an antisymmetric stretch of linear C$_{13}$. The clusters were produced in a supersonic molecular beam source, and a tunable diode laser spectrometer was used to record the spectrum. (Reprinted from ref 36. Copyright 1994 American Association for the Advancement of Science.)

80 in the P-branch and 74 in the R-branch were observed. The spectrum was characteristic of a centrosymmetric linear carbon cluster in a nondegenerate vibronic state, since only even-numbered rotational states were observed, and only P- and R-branch transitions were present. Molecular parameters obtained from analysis of the data are shown in Table 12. By assuming that the carrier of these transitions was the linear C$_{13}$ carbon cluster, an average carbon–carbon bond length of 1.2770(5) Å could be calculated from the ground-state rotational constant. C$_{13}$ is the only cluster that reproduces the bond length within the range of about 1.27 and 1.30 Å expected for a cumulated double bond. Observation of a linear carbon cluster of this size with a sufficient number density to be detected in a direct absorption experiment was surprising in light of theoretical predictions that the most stable form of these clusters should be cyclic. Hutter et al. found the cyclic isomer of C$_{13}$ to be more stable than the linear form by 20–30 kcal/mol using density functional theory. This result was consistent with the more recent study by Martin et al., cited above, who found the ring form to be favored by 28 kcal/mol using the B3LYP functional. Bleil et al. calculated relative isomer energies of linear and cyclic C$_{13}$ at the MP2/6-31G$^*$ level. The cyclic minimum was found to be a distorted planar ring of C$_{2v}$ symmetry and was only 6.8 kcal/mol lower in energy than the $1\Sigma_g^+$ linear isomer. Thus, under laser vaporization conditions, these authors predicted that entropy would favor formation of the linear chain.

Vibrational frequencies were calculated for the linear isomer by Blie et al., at the MP2 level, at the CASSCF level by Martin et al., and at the B3LYP/DFT level by Martin et al. At the CASSCF-(8/8)/cc-pVDZ level, two extremely intense infrared active antisymmetric stretch modes were calculated to occur in the region of the observed spectrum. These were the $v_9$ and the $v_{12}$ transitions at 2003 and 1843 cm$^{-1}$ respectively. By using a scaling factor of 0.93, derived from C$_9$, the $v_9$ transition of C$_{13}$ would be predicted to occur near 1850 cm$^{-1}$, which is somewhat close to the measured band origin of 1809 cm$^{-1}$. However, at the B3LYP level, there were no scaled frequencies that resembled the experimental result. The closest predictions were 1944 ± 16 cm$^{-1}$ and 1666 ± 14 cm$^{-1}$. Previously it was found that vibrational frequencies calculated using the B3LYP functional are in excellent agreement with more sophisticated CCSD(T) results for the smaller clusters, whereas the CASSCF methods were found to produce artifacts. Therefore, Martin et al. suggested that the experimental frequency may be due to a Fermi-type resonance. This would not be too surprising given the high density of states for such a large molecule.

2. Photoelectron, Optical, and Infrared Spectroscopy

C$_{11}$ was observed in the anion photoelectron spectra of Arnold et al. Three vibrational peaks, consistent with linear to linear transitions of the anion and the neutral, were measured, although no vibrational assignments were given. Broad, unresolved structure was also observed and was interpreted as transitions involving cyclic isomers for the anion and/or the neutral. Frievogal et al. observed electronic spectra of mass selected clusters deposited in a solid Ne matrix that were assigned to $2\Sigma^+_g-X\Sigma^+_g$ vibronic transitions of linear C$_{12}$ and C$_{14}$. The origin bands fit on a linear plot of the C$_4$ through C$_{10}$ origins. However, recent experiments have shown that these assignments were in error and were actually due to the (2)$\Pi-$X$\Pi$ transitions of the corresponding anions. To date, there is no conclusive experimental data to characterize the even-numbered neutral carbon clusters larger than C$_{10}$. The odd-numbered C$_{11}$, C$_{13}$, and C$_{15}$ clusters have been observed via their $2\Sigma^+_g-X\Sigma^+_g$ electronic absorption spectra in Ne matrices.

Frievogal et al. assigned two infrared absorption transitions at 1938.6 and 1853.4 cm$^{-1}$ of mass-
selected C$_{11}$ in a Ne matrix to the $\nu_7$ and $\nu_9$ antisymmetric stretch vibrations of linear C$_{11}$. A band at 2003.9 cm$^{-1}$ was tentatively assigned to linear C$_{12}$.

D. Large Carbon Cluster Ions

As already pointed out, production of neutral carbon clusters is often accompanied by the formation of carbon cluster ions, which are important in growth and annealing processes. Experimentally, larger carbon cluster ions have been studied extensively using various mass spectrometric techniques, including gas-phase ion chromatography$^{231-233}$ and ion–molecule reactivity studies.$^{239}$ In addition, photoelectron spectroscopy has been used to study carbon cluster anions as large as C$_{20}$. Optical spectra have been recorded for mass-selected anions in Ne matrices as large as C$_{20}$.$^{46}$

1. Ion Mobility Studies

Gas-phase ion chromatography has recently emerged as the most direct approach for obtaining structural information about carbon cluster ions larger than C$_{10}$. von Helden et al. reported studies on the structures and reactivities of carbon cluster cations from C$_6^{+}$ to C$_{84}^{+}$.$^{242,243}$ These authors identified several different families of structures that appear as the cluster size increases. For C$_7^{+}$ through C$_{10}^{+}$, linear chain structures coexisted with monocyclic rings.$^{241-243,260}$ As mentioned above, annealing studies showed that the ground states of these clusters were the ring forms, although linear chains were also present due to entropic considerations. The chain isomer disappeared at C$_{10}^{+}$, while planar monocyclic rings were the only isomers present for C$_{10}^{+}$ through C$_{20}^{+}$. As the cluster size increased beyond C$_{20}^{+}$, several different isomers were found to coexist. The mobilities of these isomers were consistent with planar monocyclic, bicyclic, and tricyclic rings. Above C$_{30}^{+}$, closed cage fullerene structures were also present, as well as a graphicitic fragment. For clusters larger than C$_{40}^{+}$, fullerenes became the dominant structures for even-numbered clusters and were the only isomers present above C$_{60}^{+}$. For the odd-numbered clusters, closed cage fullerenes dominated above C$_{49}^{+}$, although ring isomers continued to coexist with the cages at larger sizes. Annealing studies indicated that, of the planar rings in the C$_{20}^{+}$ to C$_{40}^{+}$ size range, the monocyclic isomers were the most stable.$^{286,289,290,293}$ It was also found that fullerenes could be formed from larger ring isomers after C, C$_2$, or C$_3$ dissociation.$^{287,288}$ Graphicitic fragments were a very minor component of the isomer distribution for C$_{20}^{+}$ to C$_{40}^{+}$, and "pentagon road" structures were not observed. Figure 27 plots the ion mobilities observed for the different cation isomers as a function of cluster size. This figure illustrates the cluster size ranges in which each kind of isomer is observed.

For the anions, these same families of structures were also observed, although there were differences in the relative isomer abundances and size distributions.$^{227,239}$ Figure 28 displays the ion mobilities as a function of cluster size for the anions. One of the differences between the ion mobility studies of the anions and those of the cations was in the size distribution of the linear chains. Linear isomers were found to coexist with monocyclic rings for C$_{10}^{+}$ all the way up to C$_{30}^{+}$, while the monocyclic ring isomers were not present for clusters smaller than C$_{10}^{+}$. Annealing studies showed that cyclic isomers were clearly favored for C$_{15}^{+}$ and larger anions and became the dominant structure by C$_{20}^{+}$. The annealing results for C$_{10}^{+}$ to C$_{15}^{+}$ were somewhat inconclusive, as discussed previously for C$_{10}^{+}$. Another surprising result of the anion studies was the low prominence of fullerene structures. Small fullerene peaks began to appear at C$_{36}^{+}$, but the fraction of these structures in the isomer distributions remained very low for all clusters. Even for C$_{60}^{+}$, the distribution was dominated by planar rings, with the fullerene accounting for less than 20% of the isomers. Of course this is entirely dependent upon the conditions under which the clusters were formed and may or may not reflect a reduced stability for the fullerene anions, relative to the ring isomers.
2. Ion–Molecule Reactivity Studies

Prior to the development of gas-phase ion chromatography, the most direct experimental data on the structures of cluster ions came from chemical reactivity studies. As already discussed, reactivity studies provided the first evidence for the existence of cyclic isomers of C$_7^+$, C$_8^+$, and C$_9^+$;$^{257,258}$ Parent and Anderson recently reviewed this area of research on metal and semimetal clusters, including carbon clusters.$^{259}$ Fourier transform ion cyclotron resonance (FT-ICR) spectrometry or guided ion beam techniques are typically used to react a mass selected carbon cluster with a reactant gas. From the measured reaction cross sections, it is possible to differentiate between, for example, reactive open-shell clusters ions such as linear chains, and less reactive cyclic species. These studies of course provide much useful information about the ion–molecule chemistry of carbon cluster ions. In recent years, carbon cluster cation structural and reactive properties have been investigated by reactions with such species as H$_2$, O$_2$, N$_2$O, benzene, naphthalene, nitriles, chloropropenes, and polyaromatic hydrocarbons. Pozniak and Dunbar recently showed that C$_{10}^+$ to C$_{24}^+$ ions whose cyclic isomers satisfied the conditions for aromaticity were less reactive than the other ions in this size range.$^{302}$

In some of these studies, information about the neutral structures was obtained by seeding the reactant in the carrier gas of a laser vaporization–supersonic expansion source.$^{294–296}$ Neutral species formed in the expansion were then ionized and observed using time-of-flight mass spectrometry. Long polyacetylenic chains (HC$_n$=H, n $\leq$ 40) were thought to be present with H$_2$ as the reactant gas, leading to the conjecture that neutral carbon chains of this size may be forming. Lagow et al.$^{34}$ introduced CF$_3$ and CN radicals into a fullerene synthesis chamber and found evidence for the formation of stable polyacetylenic carbon chains up to 300 atoms in length, stabilized by free radical end-capping groups. Furthermore, these authors found that in the presence of these free radical capping groups, fullerene synthesis was suppressed in favor of long carbon chains. Therefore, they speculated that long carbon chains are the main precursors to fullerene formation and that these chain species may be responsible for the peaks attributed to polycyclic rings in the ion mobility experiments. An alternative explanation might be that the capping groups actually suppress the formation of polycyclic ring structures, which, in turn, prevents the onset of fullerene formation. This latter explanation is more consistent with the body of evidence compiled by Bowers, Jarrold, McKelvany, and their co-workers, discussed above.$^{287,288,291,292}$

3. Photoelectron Spectroscopy

Yang et al. measured photoelectron (PE) spectra of carbon cluster anions as large as C$_{84}^-$. The most significant result of this study was the observation of an abrupt change in the electron affinity at C$_{10}^-$, which was taken as evidence for a linear to cyclic transition. More recent measurements by Hands- chuh et al. supported this observation.$^{273}$ These authors measured PE spectra of C$_{5}$ to C$_{70}$ clusters produced by laser vaporization of graphite, followed by annealing of the clusters in a He discharge. This, according to the authors, ensured that all clusters studied in the PE experiment were present in their most stable structures. Vibrationally resolved PE measurements were consistent with monocylic rings for even-numbered C$_{10}$ to C$_{18}$, bicyclic rings for C$_{20}$, C$_{24}$, and C$_{28}$, and fullerenes for even-numbered clusters larger than C$_{30}$.$^{3}$ The results for C$_{10}$, C$_{12}$, and C$_{14}$ somewhat conflict with the observations of Bowers and co-workers, who found linear chains to dominate for these clusters upon annealing.$^{227}$ These conflicting results further underscore the extreme sensitivity to experimental conditions of the carbon cluster anion isomer distribution.

4. Electronic and Infrared Absorption Spectroscopy

As has already been discussed, Maier and co-workers recently developed a technique whereby mass-selected carbon cluster anions are deposited from the gas phase into a low temperature (4 K) Ne matrix.$^{207,213,214}$ Electronic absorption spectra can then be recorded for the anion and, after UV irradiation of the matrix, the corresponding neutral cluster. Several $^2\Pi$–$^2\Pi$-type bands for linear C$_{11}^-$ and even-numbered linear C$_{12}^-$–C$_{30}^-$ have been observed.$^{207,213,214}$ In addition, two infrared absorption transitions at 2012.6 and 1819.3 cm$^{-1}$ were observed for mass-selected C$_{12}^-$ that correlated in intensity with the electronic band and disappeared upon UV irradiation.$^{228}$ Therefore, these transitions were assigned as antisymmetric stretch vibrations of linear C$_{12}^-$. 

XV. Conclusion

In their 1989 review article, Weltner and Van Zee stated that “the present knowledge of C$_n$ molecules and their ions is almost a monotonically decreasing function of n”.$^3$ This is probably still the case, although the width of the decay has increased significantly in recent years. C$_3$ is now extremely well-characterized in its ground and several excited electronic states.$^{39,40}$ and steps have now been taken to characterize this cluster in the interstellar medium.$^{5,6}$ Very precise structural information now exists for the ground electronic states of linear C$_{4}$, C$_{7}$, C$_{9}$, and C$_{13}$ from gas-phase infrared laser spectroscopy experiments.$^{35–38,236}$ Similar information for the cyclic isomers in this size range would be of great value. Accurate vibrational energies for all of the linear clusters in the C$_{4}$–C$_{9}$ size range, as well as a few vibrational frequencies for linear C$_{10}$–C$_{13}$ now exist from high-resolution laser spectroscopy measurements,$^{46}$ as well as from infrared absorption of carbon clusters in cryogenic matrices.$^{113,228}$ More accurate ab initio techniques have been applied to the cyclic isomers of these clusters, providing more reliable guidance to experimentalists trying to detect and characterize these species.$^{58,71–73,271}$ Electronic absorption$^{46}$ and mul-
C5 using infrared CRLAS, 309 and Maier and co-
states of linear carbon clusters and their anions as
electronic absorption spectra of C6H radicals produced
workers have observed rotationally resolved elec-
bond discharge method of Kra¨tschmer et al.18 Despite the
be obtained in bulk quantities by the carbon arc
further applications of CRLAS to
studies in the years to come, will clearly be needed
characterization of carbon clusters by high-resolution
Such an endeavor would almost certainly require new
spectroscopy technique that holds great promise for
fullerenes, as well as nanoscale carbon materials like
“buckytubes,” in a carbon arc. With the continued
characterization of carbon clusters by high-resolution
spectroscopy, we hope to eventually be able to moni-
tor in situ the individual species involved in the
carbon arc synthesis, and thereby contribute to a
more detailed understanding of the kinetics involved.
Such an endeavor would almost certainly require new
experimental techniques, since currently existing
methods would not have the sensitivity to carry out
such measurements. A new direct absorption spec-
troscopy technique that holds great promise for future
developments in the study of small carbon
custers is cavity ringdown laser absorption spectro-
copy (CRLAS)306–309 CRLAS is more sensitive than
conventional direct absorption spectroscopy tech-
niques and is broadly tunable from the mid-IR to the
UV. Two very recent studies underscore the potentia-
of CRLAS in the study of small carbon clusters.
provencal et al. greatly expanded the number of
observed rovibrational transitions in the v3 band of
C5 using infrared CRLAS,309 and maier and co-
workers have observed rotationally resolved elec-
tronic absorption spectra of C6H radicals produced
in a pulsed discharge source using CRLAS at visible
wavelengths.310 Further applications of CRLAS to
the study of small carbon clusters, as well as the
development of new experimental and theoretical
methods in the years to come, will clearly be needed
to solve the challenging problems that still remain
in carbon cluster research.

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XVII. References

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