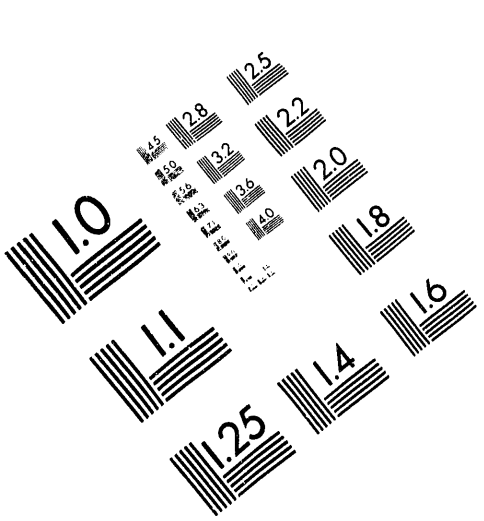

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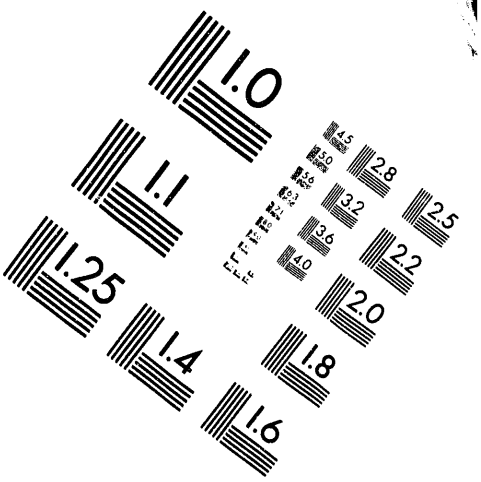

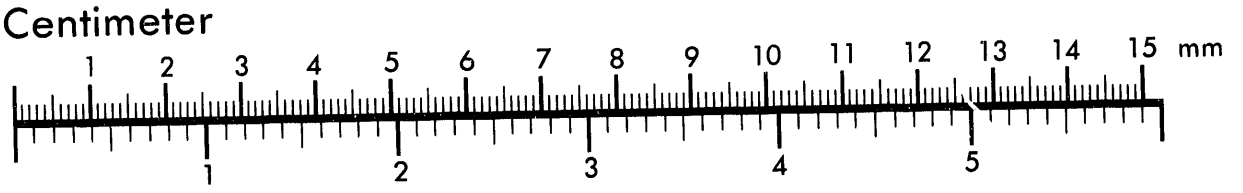

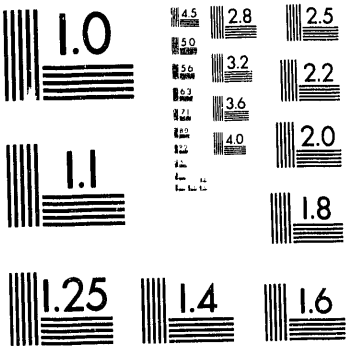

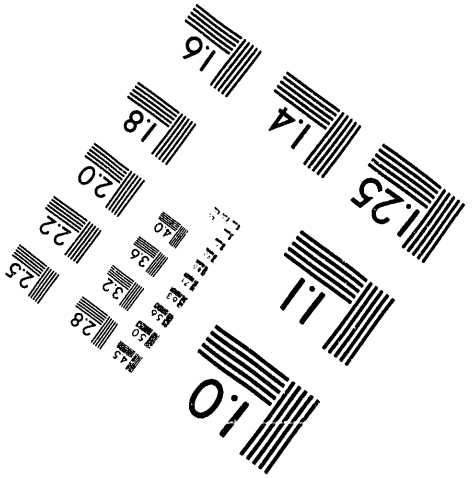

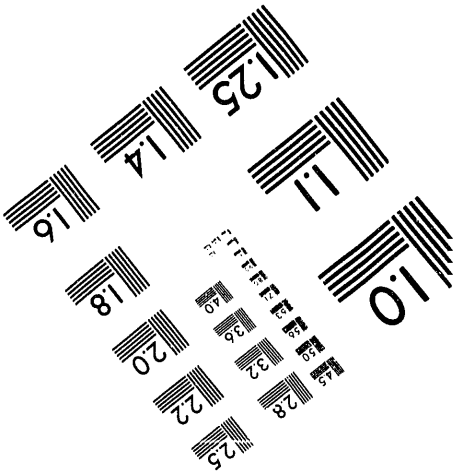

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NEGATIVE ION FORMATION IN SMALL CARBON CLUSTERS

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ABSTRACT

Laser ablation of graphite into a rare gas supersonic jet has been used to generate C_m clusters (both neutral and ionic) in the size range $m \leq 30$. Negative ions produced by three different mechanisms have been studied: (1) ion formation during the ablation process, (2) low energy electron attachment (Rydberg electron transfer) to neutral clusters, and (3) charge transfer from ground state rubidium atoms to neutral clusters. The C_m^- distributions observed for the three cases are distinctly different, providing insights into the structures, stabilities, and electron attachment dynamics of small carbon clusters.

INTRODUCTION

The study of gas phase atomic clusters has recently become one of the most prolific fields in chemical physics. Laser ablation has played a pivotal role in the development of the field. The generation of "large" atomic clusters during laser ablation of a solid target was first demonstrated by Berkowitz and Chupka,[1] who observed neutral carbon clusters (as large as C_{15}) emitted from a graphite target irradiated by a pulsed ruby laser. In 1981, Smalley and coworkers[2] coupled the techniques of laser ablation and seeded supersonic jet expansion, introducing a versatile method for producing cold, intense beams of clusters of various composition, containing atoms of any element in the periodic table. Of the elements studied so far, clusters of carbon have perhaps received the most attention. Carbon molecules are particularly interesting due to (1) their unique and fascinating structural and spectroscopic properties, (2) their importance in astrophysical processes, and (3) their role in combustion processes and soot formation.[3] The generation of carbon-containing molecules by laser ablation has also led to the discovery of new materials, such as fullerenes[4] and metallo-carbohedrenes.[5] Despite considerable experimental and theoretical progress, much is still unknown about the structures, properties, growth mechanisms, and reactivities of carbon clusters. In the present paper, we present results on negative ion formation in small carbon clusters.[6] Possible relations between the structures, stabilities, and electron attachment dynamics of the clusters are discussed.

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EXPERIMENTAL

The experimental apparatus has been described previously.[6] A carbon cluster beam was produced using a laser vaporization/supersonic jet source, in which a rotating graphite rod was vaporized by the 532 nm second harmonic output of a Nd:YAG laser. The vaporized material was entrained in a pulse of helium or argon gas from a pulsed valve and allowed to cool and condense during its passage through a 1.6 mm diameter, 11.1 mm long channel prior to expansion into vacuum and collimation into a beam. The C_m cluster beam was crossed at 90° with a collimated effusive beam of Rb atoms between two parallel mesh grids in the acceleration region of a linear time-of-flight mass spectrometer (TOFMS), whose axis was orthogonal to both molecular beams. Rubidium atoms were excited to *ns* or *nd* Rydberg states by resonant two-color excitation using two independently tunable dye lasers pumped by a single nitrogen laser. Collisions between neutral C_m clusters and Rb Rydberg atoms were allowed to proceed in a field-free region for a specified time (typically 1-10 μs) after which positive or negative ions formed during the collisions were accelerated into the TOFMS by applying a voltage pulse to one of the grids. By flagging various combinations of the lasers and Rb beam, we are able to obtain mass spectral distributions of C_m^- ions produced (a) directly in the vaporization process, (b) by Rydberg electron transfer, and (c) by electron transfer from ground state Rb atoms.

RESULTS AND DISCUSSION

A typical mass spectrum of C_m^- ions produced directly in the laser vaporization/supersonic jet source (for a helium expansion) is shown in Fig. 1. For $m \geq 10$, we observe a strong odd-even alternation in intensity (odd > even) with distinct "magic numbers" at m = 17, 21, and 25. Several spectra obtained under similar conditions also show enhanced intensity for m = 13 and 29. The intensity distribution for $m > 10$ exhibits a strong correlation with ultraviolet photoelectron spectra and electron affinities (*EA*s) of the carbon clusters,[7] both of which exhibit a clear fourfold periodicity. The *EA*s exhibit a strong odd-even alternation (odd > even) with m = 13, 17, 21, 25, and 29 having the highest *EA*s in each four-atom progression. Yang *et al.*[7] interpreted these trends as strong evidence that

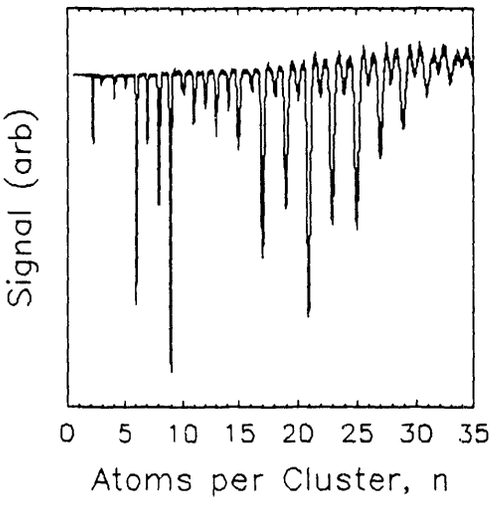

Figure 1. Mass spectrum of C_n^- ions produced directly in the laser vaporization/supersonic jet source.

clusters with $m > 10$ exist predominantly as monocyclic rings at low temperatures. The stabilities of molecules and ions with monocyclic ring structures can be understood by simple bonding considerations, analogous to Hückel's "$4m+2$ rule" for cyclic hydrocarbons.[8,9] The most stable clusters are those whose highest occupied molecular orbitals (HOMOs) are fully occupied. For monocyclic rings, each carbon atom contributes two electrons to the π bonding orbitals and the HOMOs are completely filled for neutral clusters which have $4m+2$ atoms. Due to the extra electron present for negative ions, those ions with $4m+1$ atoms will have completely filled HOMOs and will be more stable.[9] Negative ions with $4m+1$ atoms (i.e., m = 13, 17, 21, 25, etc.) are indeed the clusters appearing with greatest intensity in Fig. 1. The present results thus suggest that, for our source conditions, the intensities of C_m^- ions produced directly in the vaporization process are correlated with the thermodynamic stabilities of the ions, and that monocyclic ring structures are energetically favored for cluster ions with $m > 10$.

Mass spectra of C_m^- ions produced by Rydberg electron transfer (RET) to neutral carbon clusters are shown in Fig. 2 for (a) vaporization into a helium jet and (b) vaporization into an argon jet. Both spectra were obtained for the 30*d* state of Rb. Similar distributions were obtained for several *ns* and *nd* Rydberg states ($20 \leq n \leq 40$). In all cases, the distributions were characterized by distinct magic numbers for m = 5, 10, 12, 16, and 18. It is now well known that, for large values of principal quantum number, n, rate constants for RET are directly related to rate constants for free electron attachment.[10] The Rydberg electron is, on average, far enough from the atomic ion core that the electron and the core behave as independent scatterers during a collision between the Rydberg atom and a neutral molecule. The slow Rydberg electron thus behaves essentially as a "free" low energy electron, which is easily captured by the target molecule. The negative ion signals observed for RET are dependent upon several factors, including the number densities of neutral clusters in the beam, low-energy

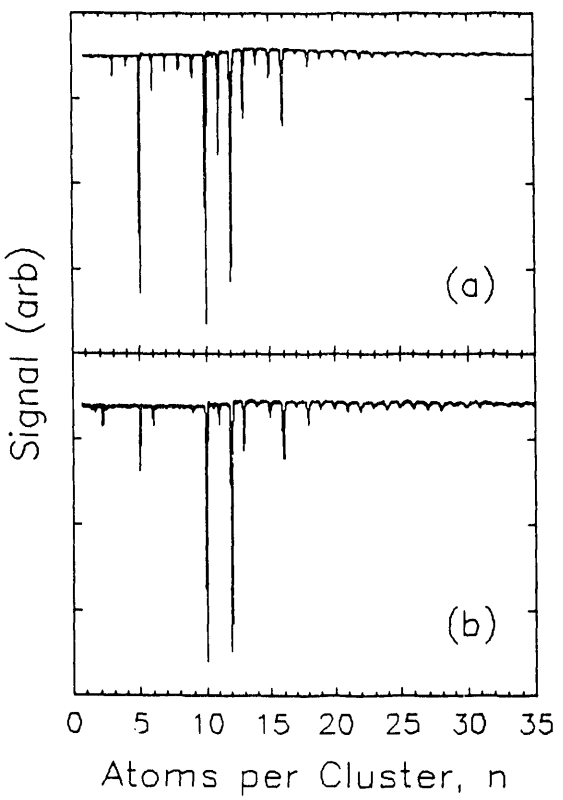

Figure 2. Mass spectra of C_n^- ions produced by RET for (a) a helium expansion and (b) an argon expansion.

electron attachment cross sections, and stabilities and lifetimes of the negative ions produced. The fact that we observe similar negative ion distributions under many different source conditions and with various carrier gases (i.e., under conditions where cluster cooling and growth are expected to be quite different) leads us to believe that the magic numbers seen in the RET mass spectra do not depend strongly upon the relative abundances of neutral carbon clusters within the beam nor upon their temperatures (internal energies). From the discussion above, it also follows that something other than ion stability is contributing to the magic numbers seen in Fig. 2. We suggest that the magic numbers seen in the RET mass spectra (i.e., m = 5, 10, 12, 16, and 18) reflect carbon clusters which have much larger cross sections for low energy electron attachment than do other clusters.[6] We have also proposed that low energy electron attachment within the vaporization/jet source may become important if the density of the carrier gas is high enough to efficiently thermalize electrons produced during laser ablation. Such a mechanism provides an intuitive explanation for magic numbers often observed in C_m^- distributions obtained from such sources, which are similar to the magic numbers we observe for RET.[6]

The relation between electron attachment cross sections and molecular properties such as structure, electron affinity, etc., are not clear. However, it is interesting to note that, in a study of electron attachment to selected hydrocarbon molecules, Frey *et al.*[11] observed large cross sections for parent ion production for low energy (<0.5 eV) electron attachment to acenaphthylene ($C_{12}H_8$) and fluoranthene ($C_{16}H_{10}$) molecules, which are polycyclic hydrocarbons. The fact that we observe enhanced signals for 12- and 16-atom carbon clusters prompts us to ponder whether pure carbon molecules with polycyclic structures, such as those shown in Fig. 3, may also have large cross sections for electron attachment. Similar polycyclic structures have been recently detected as intermediates in fullerene formation.[12]

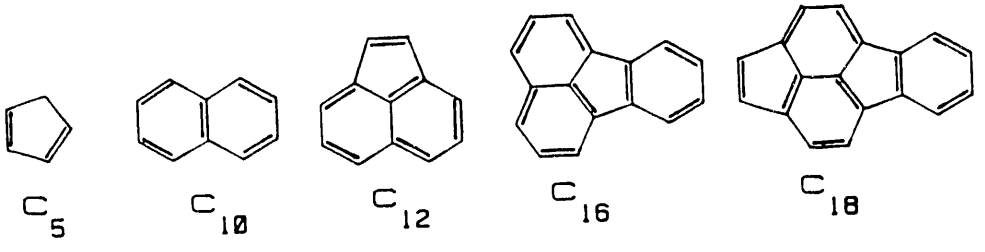

Figure 3. Examples of polycyclic structures for C_m clusters.

Mass spectra of C_m^- ions produced by charge transfer between *ground state* Rb atoms and neutral carbon clusters are shown in Fig. 4 for (a) vaporization into a helium jet and (b) vaporization into an argon jet. In contrast to the RET

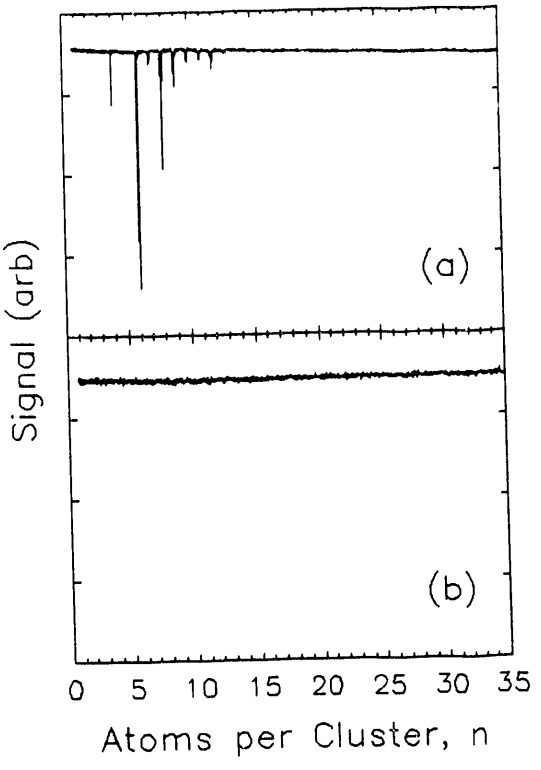

Figure 4. Mass spectra of C_m^- ions produced by charge transfer from ground state Rb atoms for (a) a helium expansion and (b) an argon expansion.

data, a significant difference is observed for the two carrier gases. No negative ions were observed for the argon expansion, even though it is clear from Fig. 2(b) that an intense neutral cluster beam was produced. We therefore conclude that the production of negative ions by charge transfer from ground state Rb atoms depends strongly upon the initial center-of-mass (CM) kinetic energy of the collision partners. Assuming that the carbon clusters are accelerated to the flow velocity of the carrier gas, the kinetic energies obtained for the two expansions are significantly different. By measuring the time delay between the vaporization laser pulse and the arrival of the clusters in the collision region, we are able to estimate the CM collision energies, E_{cm}, which are summarized in Table I. Also shown in Table I are the expected thermodynamic thresholds for negative ion formation, which are given by $E_{th} = IP(\mathrm{Rb}) - EA(C_m)$, where IP(Rb) is the ionization potential of Rb (4.176 eV), and $EA(C_m)$ are the electron affinities of the carbon clusters.[7,13] As can be seen in Fig. 4 and Table I, the C_m^- ions which appear for the He expansion are those whose CM kinetic energies exceed the thermodynamic threshold for negative ion formation. Note, however, that C_6 and C_8 have EAs which exceed the IP of Rb. For these clusters, no threshold exists for negative ion formation. C_6^- and C_8^- appear with the greatest intensity for the helium expansion; however, these ions are *not* observed for the argon expansion. From the RET results, it is certain that C_6 and C_8 clusters are present in the argon jet. It therefore appears that, although no thermodynamic threshold exists for negative ion formation for these two molecules, some sort of dynamical barrier exists which inhibits ion pair production at low kinetic energies. More detailed experimental studies of the energy dependence of the charge transfer cross sections are needed to elucidate the dynamics of these processes.

Table I. EA, E_{th}, and E_{cm} values

Molecule	EA (eV)[a]	E_{th} (eV)	E_{cm} (eV, helium)	E_{cm} (ev, argon)
C_2	3.273	0.903	0.325	0.047
C_3	1.995	2.181	0.439	0.063
C_4	3.882	0.294	0.533	0.077
C_5	2.839	1.337	0.611	0.088
C_6	4.185	- 0.009	0.677	0.097
C_7	3.358	0.818	0.733	0.105
C_8	4.379	- 0.203	0.783	0.113
C_9	3.684	0.492	0.826	0.119
C_{10}	-	-	0.865	0.124
C_{11}	3.913	0.263	0.898	0.129

[a] from Ref. 13

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