LETTERS TO THE EDITOR

The Letters to the Editor section is divided into four categories entitled Communications, Notes, Comments, and Errata. Communications are limited to three and one half journal pages, and Notes, Comments, and Errata are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 1996 issue.

COMMUNICATIONS

Evidence of small odd-numbered dianionic carbon cluster beams from a cesium-sputter negative ion source

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Evidence of odd-numbered C_n^{2-} (n=7–13) cluster beams produced in a cesium-sputter negative ion source has been observed. The minimum lifetime of smallest dianion, C_7^{2-}, is estimated to be at least 55 μs. An experiment to investigate the structure of these dianions is also described. © *1996 American Institute of Physics.* [S0021-9606(96)03431-9]

All long-lived, free, dianions observed and reported thus far consist of molecules or clusters. Dianionic molecules or clusters are more likely to be stable than doubly charged negative atomic ions, since the spatial separation of the additional two electrons can be greater for molecules and clusters, reducing the interelectron repulsion energy. By extension, the interelectron repulsion of a cluster should decrease as its size increases, so that a large cluster might be stable with more than one additional electron.

Dianions of large molecules and clusters have been observed on several occasions over the past three decades.[1–3] However, dianions of small molecules and clusters in the region where the interelectron repulsion becomes large have rarely been observed. The first observation of small dianions was reported by Schauer *et al.*[4] using a secondary ion mass spectrometer. Observation of mass-analyzed, secondary, C_n^{2-} clusters for n=7–28 produced by sputtering graphite with Cs^+ ions at impact energies of 14.5 keV were reported. The observed mass spectra exhibited an alternating pattern, with even-n clusters being more intense than odd-n clusters. Carbon-13 enriched graphite targets were also used to confirm the observations. The lifetime of the smallest dianionic cluster C_7^{2-} was estimated to be at least 10 μs, with larger clusters having correspondingly longer lifetimes. Recently, Gnaser and Oechsner[5] observed dianionic carbon clusters for n=7–22, using the same sputtering and mass analysis technique. In addition, they also observed the odd–even oscillations in their mass spectra, again with even-n clusters being more intense than odd-n clusters.

The odd–even oscillations in the mass spectra led Schauer *et al.*[4] to propose a linear geometric structure for the small dianionic clusters and a ring structure for dianionic clusters larger than C_{20}^{2-}. A subsequent theoretical investigation by Watts and Bartlett[6] could not predict a stable linear chain structure of C_n^{2-} for n=2–10 with respect to vertical or adiabatic autodetachment. A recent comprehensive theoretical investigation[7] predicted that all linear and quasi-linear geometries of C_7^{2-} are unstable with respect to electron autodetachment. This study presented the first theoretical evidence of an electronically stable free C_7^{2-} cluster. In particular, these calculations showed that C_7^{2-} is stable with respect to vertical and adiabatic autodetachment and stable with respect to all dissociation channels, when the carbon atoms are in a trigonal planar arrangement (D_{3h} symmetry). Furthermore, the triangular isomer $[C(C_2)_3]^{2-}$ was determined to be stable with respect to $[C(C_2)_3]^-$ in their separately optimized D_{3h} geometric arrangements. The $[C(C_2)_3]^-$ geometry is actually a local minimum in the potential energy surface of C_7^-. As a result, the linear isomer of C_7^- is lower in energy than its D_{3h} isomer. Results of a self-consistent field calculation with electron correlation predicted an adiabatic ionization potential of 0.45 eV. This ionization potential was defined as the total energy difference between C_7^{2-} and C_7^- in their D_{3h} geometric configurations. Studies of C_9^{2-} were also reported and indicate that it is vertically stable with respect to electron autodetachment in the C_{2v} geometry, and unstable with respect to vertical and adiabatic electron removal in the linear isomer of the $D_{\infty h}$ geometry. As a result of these calculations, Sommerfeld *et al.*[7] argued that triangular structures may emerge as the building scheme for odd-numbered dianionic carbon clusters.

The previous experimental observations of dianionic carbon clusters resulted from secondary ion production. Furthermore, the ion intensities in each observation were sufficiently small to be detected by pulse counting techniques, with count rates of 100 kHz or less. This communication presents the first evidence of the production of odd-numbered C_n^{2-} (n=7–13) ion beams formed in a cesium-sputter negative ion source. A new estimate of the minimum lifetime of C_7^{2-} is presented as well as a description of an experiment to investigate the structure of these clusters.

The cesium-sputter negative ion source utilized in the present experiment is a commercially manufactured source.[8] Positively charged cesium ions were produced by thermally ionizing cesium atoms with a cylindrical-geometry tungsten ionizer heater, and were subsequently accelerated toward a graphite pellet (target). The cesium ion beam forms a thin

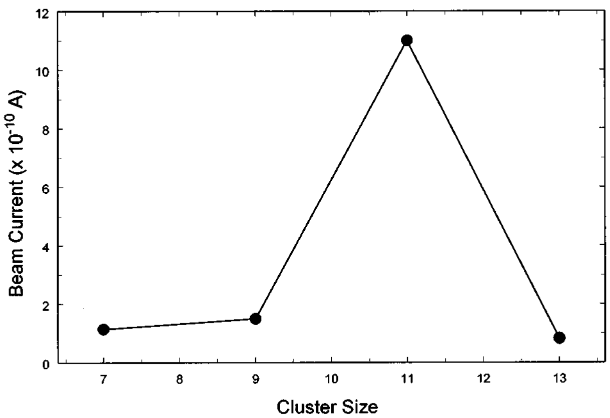

FIG. 1. Mass spectra of the dianionic carbon clusters produced in a cesium-sputter negative ion source. The beam energy was 10 keV and the sputter probe voltage was 2.0 kV.

coating on the target and sputters matter from the graphite pellet. Particles that are sputtered from the surface of the target produce low velocity neutrals that can become negatively charged as they leave the cesiated surface of the carbon pellet. Negative ions that are produced in the source, exit through an aperture and are further accelerated to ground potential as they travel toward an extraction electrode. Typically, the current through the ionizer was 21.5 A. The acceleration energy (sputter probe voltage) of the cesium ions ranged from 1.0–3.8 keV. This energy range yielded maximum beam intensities for each C_n^{2-} species observed. Cluster ions produced in the source were accelerated to energies ranging from 4–40 keV. After traveling approximately 2.4 m, the beam entered a 90° bending magnet for mass analysis. The resolution of the mass-analyzer was approximately 1%. Since the mass-to-charge ratio of the even-numbered dianions could not be distinguished from anions with half the dianionic mass, their production yields could not be determined. The intensity of the mass-analyzed negative ion beam was measured with an insertable Faraday cup placed 2.8 m from the exit aperture of the magnet. The ion beamlines preceding and following the magnet included electrostatic steering and focusing elements, in order to maximize the ion beam current in the insertable Faraday cup.

Figure 1 depicts a representative sample of odd-n C_n^{2-} mass spectra obtained with the cesium-sputter negative ion source. Observed dianionic cluster sizes ranged from $n=7$–13 with beam intensities of approximately 10^{-10} A (~300 MHz count rate). The intensity of ions produced in the cesium-sputter negative ion source is significantly higher than those previously observed as secondary ions.[4,5] The observed peaks in the mass spectra are unique to the graphite pellet. For the 4 keV C_7^{2-} beam that traversed the 5.2 m long apparatus, the time of flight yielded a minimum estimated lifetime of 55 μs. Larger dianions produced at this energy will have longer minimum lifetimes. A mass analysis of C_n^- ions for $n=1$–60 revealed a similar structure to those produced in an excimer laser vaporization/supersonic expansion source.[9] In addition, the mass spectrum revealed characteristic C_n^- structural transitions from linear geometries to monocyclic rings, and finally to three-dimensional structures.[10–12] This suggests that the cesium-sputter negative ion source may produce negative molecular and cluster ions that have similar vibrational populations as those produced in a supersonic expansion source. Evidence for a long-lived, free, C_5^{2-} cluster has also been observed. Beam intensities of approximately 10^{-10} A have been observed for $m/q=30$ amu with a graphite sputter target in the source. No theoretical evidence for long-lived, free, C_5^{2-} ions have been reported. Further investigations are required to distinguish C_5^{2-} from possible contaminants in the source such as NO^- and SiH_2^-.

An apparatus has been developed to probe the structure of the dianionic carbon clusters with the laser photoelectron spectroscopy (LPES), and the photoelectron–photoion coincidence techniques. The experiments will be performed by crossing a beam of C_n^{2-} ions with a photon beam from a continuous argon-ion laser. The resulting photoelectrons will be energy-analyzed by a 160° spherical-sector analyzer. Photoions resulting from the detachment process will be deflected through a vertical electrostatic quadrupole and detected with a pair of microchannel plates in the chevron configuration. The purpose of the electrostatic quadrupole deflector is to monitor the parent and fragment ions resulting from the photodetachment process. Coincidences between detected photoelectrons and photoions will be measured. The goal of this project is to determine the vertical detachment energy (VDE) of dianionic carbon clusters, and probe the geometry of the dianionic carbon clusters by investigating the photofragmentation channels of C_n^{2-}.

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