Carbon Cluster Ions from Low- and High-Temperature Glassy Carbon, Highly Oriented Pyrolytic Graphite, and Polycrystalline Graphite

Michael A. May, Michael E. Huston, Matthew R. Callstrom,* and Alan G. Marshall*,†

Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210

Received November 10, 1992. Revised Manuscript Received February 9, 1993

Carbon cluster ions have been produced by pulsed Nd:YAG laser desorption of four sp^2-hybridized carbon solids: glassy carbon-6 (GC-6), glassy carbon-25 (GC-25), highly oriented pyrolytic graphite (HOPG), polycrystalline graphite, and the oligomeric precursor to GC-6, poly(phenylenediacetylene). The desorbed ions were detected by Fourier transform ion cyclotron resonance mass spectrometry. Under similar laser and mass spectrometry conditions, polycrystalline graphite yielded abundant fullerene ions (C_{44}^+ to C_{124}^+). GC-6, synthesized by a low-temperature route, gave increased ion populations from C_{14}^- to C_{25}^- relative to conventional GC-25. Laser desorption of the organic precursor, poly(phenylenediacetylene), yielded fullerenes from C_{60}^+ to C_{150}^+ in positive-ion mode, and C_3^- to C_{10}^- in negative-ion mode. The present results show that (a) pulsed laser desorption of polycrystalline graphite produces a higher yield of fullerene cations compared to other sp^2-type carbon solids, (b) low-mass carbon cluster ions from C_{14} to C_{30} are consistently produced from all four carbon solids as positive ions but not as negative ions, and (c) no fullerene anions are produced from any of the carbon solids under these experimental conditions, implying different formation mechanisms for positive and negative carbon cluster ions.

Introduction

Carbon-based materials are important for their utility as electrodes in a variety of electrochemical systems. Although most carbon electrodes used for electrochemistry are synthetic graphites, a variety of sp^2-hybridized carbon materials with different microcrystalline structures exist, including glassy carbon (GC), highly oriented pyrolytic graphite (HOPG), and polycrystalline graphite. The microcrystalline structure of carbon solids critically affects their physical properties and their capacity to function as electrodes.[1]

Recently, Callstrom and co-workers discovered a low-temperature route (600 °C) to glassy carbon materials[2-6] as opposed to the preparation of GC by conventional thermolysis of polymeric materials at temperatures of 1800–3000 °C.[7-14] This low-temperature route to glassy carbon solids has allowed the incorporation of dopants into the carbon matrix, including nitrogen, silicon, fluorine, and platinum. The platinum-doped glassy carbon materials exhibit excellent electrocatalytic behavior.[2]

Laser desorption mass spectrometry (LD/MS) has been widely applied to the analysis of solid carbon samples, particularly after the identification of C_{60}^+ in 1984.[15,16] In addition to graphite[15-17] and diamond film,[18] LD/MS studies have produced and detected fullerene ions from various precursors including polycyclic aromatic hydrocarbons,[19] polyimide,[20] ethylene–tetrafluoroethylene copolymer,[21] $C_{8n}O_{2n}$-type carbon oxides,[22] and coal-derived coke.[23] Carbon clusters of size up to C_{30} have long been observed in the laser desorption mass spectra of graphite[24-28] and carbon "foil",[29-31] but mass spectrometry of

---

* To whom correspondence may be addressed.

† Also a member of the Department of Biochemistry.

(1) McCreery, R. L. In *Electroanalytical Chemistry: A Series of Advances*; Bard, A. J., Ed.; Marcel Dekker: New York, 1991; Vol. 17, pp 221–374.

(2) Pocard, N. L.; Alsmeyer, D. C.; McCreery, R. L.; Neenan, T. X.; Callstrom, M. R. *J. Am. Chem. Soc.* **1992**, *114*, 769–771.

(3) Callstrom, M. R.; McCreery, R. L.; Alsmeyer, D. C.; Neenan, T. X. *J. Am. Chem. Soc.* **1990**, *112*, 4954–4956.

(4) Neenan, T. X.; Bachman, B. J.; Callstrom, M. R.; McCreery, R. L.; Alsmeyer, D. C. *Br. Polym. J.* **1990**, *23*, 171–177.

(5) Callstrom, M. R.; McCreery, R. L.; Alsmeyer, D. C.; Neenan, T. X. *ACS Prepr., Polym. Mater. Sci. Eng.* **1989**, *61*, 921–923.

(6) Neenan, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M. *Macromolecules* **1988**, *21*, 3525–3527.

(7) Yamada, S.; Sato, H. *Nature* **1962**, *193*, 261–262.

(8) Davidson, H. W. British Patent No. 860342, 1961.

(9) Cowlard, F. C.; Lewis, J. C. *J. Mater. Sci.* **1967**, *2*, 507–512.

(10) Lopatto, Y. S.; Khakimova, D. K.; Nikitina, V. K.; Avdeenko, M. A.; Plavnik, G. M. *Dokl. Akad. Nauk. SSSR* **1974**, *217*, 100–103.

(11) Jenkins, G. M.; Kawamura, K. *Polymeric Carbons: Carbon Fibre, Glass, and Char*, University Press: Cambridge, 1976.

(12) Fitzer, K.; Mueller, K.; Schaefer, W. In *Chemistry and Physics of Carbon*; Thrower, P. A., Ed.; Marcel Dekker: New York, 1971; Vol. 7.

(13) Cacha, L.; Rozploch, F.; Wlosinski, W. Polish PL. 130425 B1.

(14) Eckert, H.; Levendis, Y. A.; Flagan, R. C. *J. Phys. Chem.* **1988**, *92*, 5011–5019.

(15) Rohlfing, E. A.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* **1984**, *81*, 3320–3322.

(16) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162–163.

(17) Becker, S.; Dietze, H.-J.; Pompe, W. *Z. Chem.* **1986**, *26*, 453–454.

(18) McElvany, S. W.; Dunlap, B. I.; O'Keefe, A. *J. Chem. Phys.* **1987**, *86*, 715–725.

(19) Lineman, D. N.; Somayajula, K. V.; Sharkey, A. G.; Hercules, D. M. *J. Phys. Chem.* **1989**, *93*, 5025–5026.

(20) Creasy, W. R.; Brenna, J. T. *Chem. Phys.* **1988**, *126*, 453–468.

(21) Creasy, W. R.; Brenna, J. T. *J. Chem. Phys.* **1990**, *92*, 2269–2279.

(22) Rubin, Y.; Kahr, M.; Knobler, C. B.; Diederich, F.; Wilkins, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 495–500.

(23) Greenwood, P. F.; Dance, I. G.; Fisher, K. J.; Willet, G. D.; Pang, L. S. K.; Wilson, M. A. *Org. Mass Spectrom.* **1991**, *26*, 920–922.

(24) Dorenburg, E.; Hintenberger, H. *Z. Naturforsch.* **1959**, *14a*, 765–767.

(25) Dorenburg, E.; Hintenberger, H.; Franzen, J. *Z. Naturforsch.* **1961**, *16a*, 532–534.

0897-4756/93/2805-0648$04.00/0

glassy or pyrolytic carbon solids is scarce.[32,33]

The high mass-resolving power, selective ion ejection, and ion chemistry capabilities of Fourier transform ion cyclotron resonance mass spectrometry (FT/ICR/MS)[34–46] have stimulated numerous laser desorption/carbon cluster observations.[18,23,47–52] For example, carbon cluster positive ions produced by laser desorption FT/ICR/MS of HOPG (mass to charge ratio range, $70 < m/z < 400$) were recently reported.[53] Here we compare GC-6, GC-25, basal plane HOPG, polycrystalline graphite, and the precursor to GC-6, poly(phenylenediacetylene), by pulsed laser desorption FT/ICR/MS, to see how carbon cluster ion distributions depend on the various sp^2-type carbon structures.

Experimental Section

Glassy carbon-6 (thermally treated to 600 °C, see Figure 1) was synthesized by heating poly(phenylene diacetylene) to 330 °C under pressure followed by vacuum heat treatment to 600 °C at the rate of 1 °C min^{-1}.[2–6] The resulting GC-6 disks measured 10-mm-o.d. by 1 mm thick. The Raman spectrum of GC-6 confirmed the microcrystalline structure of glassy carbon, with characteristic bands near 1590 and 1350 cm^{-1}. Additionally, GC-6 exhibited similar density (1.5 g cm^{-3}), Young's modulus (28 500 MN m^{-2}), and shear modulus (10 800 MN m^{-2}) to conventional GC-25 (1.5 g cm^{-3}, 29 400 MN m^{-2}, and 12 000 MN m^{-2}, respectively). LD/MS was performed on one face of a GC-6 disk. A disk of poly(phenylene diacetylene) measuring 10 mm by 1 mm was fabricated by compressing the powder for laser desorption. (**Warning**: poly(phenylenediacetylene) is a highly reactive material and it should be handled and stored with care.) GC-25 (thermally treated to 2500 °C) was obtained from Atomergic Chemetals Corp. (Farmingdale, NY) as 15-mm-o.d. by 2-mm-thick disks. Raman spectroscopic analysis of GC-25 gave two major bands near 1590 and 1350 cm^{-1}. LD/MS was performed on one face of a GC-25 disk.

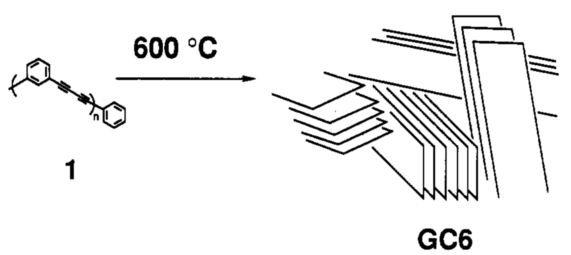

Figure 1. Schematic synthesis of GC-6 from poly(phenylene-diacetylene) precursor. Typical dimensions of the graphitic "sheets" in GC-6 are 2 × 2 nm in the basal plane and 1 nm in the perpendicular direction. The graphitic sheets are nonuniform in size, and disordered with respect to each other.

HOPG samples were obtained from Union Carbide Corp. (Parma, OH) and cut into 10 mm × 10 mm × 1 mm plates. The Raman spectrum of the HOPG sample gave bands near 1580 and 2720 cm^{-1}. A fresh basal plane surface of HOPG material was exposed prior to laser desorption by the use of Scotch tape to remove several graphitic layers. LD/MS was done on the basal plane face of an HOPG plate. Polycrystalline graphite was obtained as cylindrical rods from Carbone U.S.A. (Ultra Carbon Division, Bay City, MI) and was of "ultra F" purity. Its Raman spectrum yielded three bands near 1350, 1580, and 2710 cm^{-1}. A 6-mm-diameter rod was cut (perpendicular to the long axis) into 2-mm-thick disks, polished with 600 grit sandpaper, and washed with methanol prior to mass spectrometry. LD/MS was done on the face of a polycrystalline graphite disk.

Mass spectra were obtained with an Extrel FTMS-2000 instrument (Extrel FTMS, Madison, WI) operated at 3.02 T, equipped with dual cubic 4.763-cm ion traps, each pumped by a Helix Technology CryoTorr-8 cryopump. All mass spectra were collected at ion trap pressure below 5 × 10^{-8} Torr. The experimental event sequence was controlled by an Extrel 1280 data station, which also collected and reduced the data. Typical FT/ICR/MS parameters included a trapping potential of 1 V (+1 V for positive ions, or −1 V for negative ions), no reaction delay between the laser pulse and rf excitation, direct-mode frequency-sweep excitation (~110 V$_{(p-p)}$, swept at 1000 Hz μs^{-1}, from 20 to 1000 kHz), and 1 MHz direct-mode detection from the source trap. 128K time-domain points were collected and Fourier transformed to produce each 64K magnitude-mode mass spectrum.

A pulsed Nd:YAG laser (Continuum Inc., Santa Clara, CA, Model YG-660A) provided a beam of unseparated 1064 and 532-nm light for carbon cluster desorption. Laser-desorbed neutrals were not post-ionized. The maximum laser energy was measured to be ~300 mJ pulse^{-1} as measured by a power meter (OPHIR Optics Ltd, Wilmington, MA), and the pulse width is reported by Continuum, Inc. to be ~10 ns. The beam was focused to a 0.5-mm-diameter spot, yielding a laser power density of ~1.5 × 10^{10} W cm^{-2}. An 18-mm mechanical iris (Melles Griot, Irvine, CA) was used to control the beam diameter prior to focusing. In general the target surface was subjected to repeated laser shots (at the same spot) in order to remove any surface contaminants prior to collecting a mass spectrum. Due to pulse-to-pulse variability in the power output of the Nd:YAG laser, 10 laser shots were averaged per mass spectrum.

Results and Discussion

Carbon Electrode Solids. Laser desorption of the four carbon materials, at or above a power density of ~2 × 10^8 W cm^{-2}, gave carbon cluster ions ranging from C$_5$ to C$_{124}$ (the combined range for all four materials). The positive ion cluster distribution of each carbon material differed significantly from its corresponding negative ion cluster

---

(26) Berkowitz, J.; Chupka, W. A. *J. Chem. Phys.* **1964**, *40*, 2735–2736.

(27) Dietze, H.-J.; Becker, S.; Opauszky, I.; Matus, L.; Nyary, I.; Frecska, J. *Mikrochim. Acta* **1983**, *3*, 263–270.

(28) Knight, R. D.; Walch, R. A.; Foster, S. C.; Miller, T. A.; Mullen, S. L.; Marshall, A. G. *Chem. Phys. Lett.* **1986**, *129*, 331–335.

(29) Furstenau, N.; Hillenkamp, F.; Nitsche, R. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *31*, 85–91.

(30) Furstenau, N.; Hillenkamp, F. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *37*, 135–151.

(31) Furstenau, N. *Fresenius Z. Anal. Chem.* **1981**, *308*, 201–205.

(32) Lausevic, M.; Popovic, A.; Lausevic, Z. *Rapid Commun. Mass Spectrom.* **1990**, *4*, 515–518.

(33) Iwaki, M.; Takahashi, K.; Yoshida, K.; Okabe, Y. *Nucl. Instrum. Methods* **1989**, *B39*, 700–703.

(34) Asamoto, B.; Dunbar, R. C. *Analytical Applications of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry*; VCH: New York, 1991.

(35) Campana, J. E. *Proc. SPIE Appl. Spectrosc. Mater. Sci.* **1991**, *1437*, 138–149.

(36) Freiser, B. S. In *Bonding Energies in Organometallic Compounds*; American Chemical Society: Washington, DC, 1990; Vol. 428, pp 55–69.

(37) Ghaderi, S. *Ceram. Trans.* **1989**, *5*, 73–86.

(38) Laude, D. A., Jr.; Hogan, J. D. *Technisches Messen* **1990**, *57*, 155–159.

(39) *Lasers in Mass Spectrometry*; Lubman, D. M., Ed.; Oxford University Press: New York, 1990.

(40) Marshall, A. G.; Grosshans, P. B. *Anal. Chem.* **1991**, *63*, 215A–229A.

(41) Marshall, A. G.; Schweikhard, L. *Int. J. Mass Spectrom. Ion Proc.* **1992**, *118/119*, 37–70.

(42) Nibbering, N. M. M. *Acc. Chem. Res.* **1990**, *23*, 279–285.

(43) Nuwaysir, L. M.; Wilkins, C. L. *Proc. SPIE Appl. Spectrosc. Mater. Sci.* **1991**, *1437*, 112–123.

(44) Sharpe, P.; Richardson, D. E. *Coord. Chem. Rev.* **1989**, *93*, 59–85.

(45) Wanczek, K.-P. *Int. J. Mass Spectrom. Ion Proc.* **1989**, *95*, 1–38.

(46) Wilkins, C. L.; Chowdhury, A. K.; Nuwaysir, L. M.; Coates, M.-L. *Mass Spectrom. Rev.* **1989**, *8*, 67–92.

(47) Zimmerman, J. A.; Creasy, W. R. *J. Chem. Phys.* **1991**, *95*, 3267–3274.

(48) So, H. Y.; Wilkins, C. L. *J. Chem. Phys.* **1989**, *93*, 1184–1187.

(49) McElvany, S. W. *J. Chem. Phys.* **1988**, *89*, 2063–2075.

(50) McElvany, S. W.; Nelson, H. H.; Baronavski, A. P.; Watson, C. H.; Eyler, J. R. *Chem. Phys. Lett.* **1987**, *134*, 214–219.

(51) McElvany, S. W.; Creasy, W. R.; O'Keefe, A. *J. Chem. Phys.* **1986**, *85*, 632–633.

(52) Limbach, P. A.; Schweikhard, L.; Cowen, K. A.; McDermott, M. T.; Marshall, A. G.; Coe, J. V. *J. Am. Chem. Soc.* **1991**, *113*, 6795–6798.

(53) Liang, Z.; Ricca, T. L.; Marshall, A. G. *Rapid Comm. Mass Spectrom.* **1991**, *5*, 132–136.

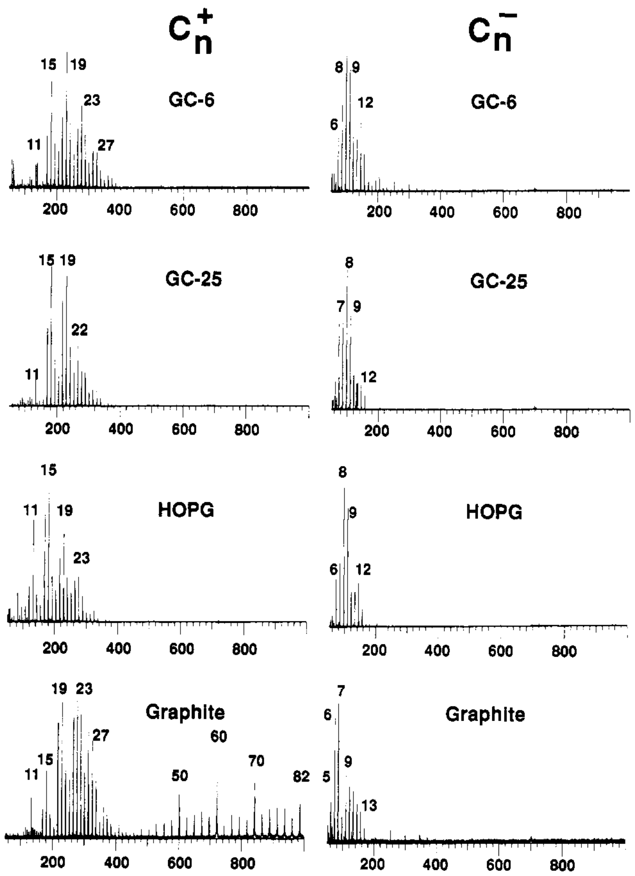

Figure 2. Positive-ion (left) and negative-ion (right) laser desorption FT/ICR mass spectra of GC-6, GC-25, HOPG, and polycrystalline graphite over the mass range $50 < m/z < 1000$. The more abundant carbon cluster ions, C_n^+ and C_n^-, are identified by their *n* values.

Table I. Positive Ion LD/FT/ICR Mass Spectra of Carbon Materials

	cluster range	abundant ions (high to low)	other ions
GC-6	C_{14}–C_{31}	C_{19}, C_{15}, C_{23}, C_{18}, C_{20}	C_{11}, $C_{23}H$
GC-25	C_{14}–C_{28}	C_{15}, C_{19}, C_{18}, C_{14}, C_{22}	C_{11}
HOPG	C_7–C_{28}	C_{15}, C_{14}, C_{11}, C_{19}, C_{18}	C_7
polycrystalline graphite	C_{10}–C_{34}	C_{19}, C_{15}, C_{20}, C_{18}, C_{14}	C_{40}–C_{124} (even)

distribution. Increasing the laser power density from 2×10^8 to 1.5×10^{10} W cm^{-2} had little effect on the relative abundances of carbon clusters from C_5 to C_{30}, although the kinetic energy of laser sputtered C_2 dimers from graphite is known to be a strong function of laser fluence under some conditions.[54] Laser desorption produced a cylindrical channel (diameter ~0.5 mm) on the carbon surfaces, where the density of carbon radicals immediately after the pulse is estimated to be $>10^{17}$ cm^{-3}. Positive and negative ion FT/ICR mass spectra of GC-6, GC-25, HOPG, and polycrystalline graphite are compared in Figure 2. Tables I and II summarize the full range of carbon clusters observed, the most abundant ions detected, and other ions of interest.

Carbon Electrode Solids: Positive Ions. Polycrystalline graphite, uniquely among the four carbon materials, yielded a bimodal carbon cluster distribution with one family from C_{10}^+ to C_{34}^+, and another composed of even-numbered fullerenes from C_{44}^+ to C_{124}^+. Figure 2 (left-hand spectra) shows these positive ion carbon clusters over the range $50 < m/z < 1000$. Table I contains a summary of the observed relative abundances for "magic number" cluster sizes (C_{11}^+, C_{15}^+, C_{19}^+, C_{23}^+, C_{60}^+, and C_{70}^+); these observations are consistent with previous work on graphite.[15,55,56]

Table II. Negative Ion LD/FT/ICR Mass Spectra of Carbon Materials

	cluster range	abundant ions (high to low)	other ions
GC-6	C_5–C_{17}	C_8, C_9, C_7, C_{12}, C_6	$C_{10}H$, $C_{12}H$, C_{21}, C_{25}
GC-25	C_5–C_{13}	C_8, C_9, C_7, C_6, C_5	
HOPG	C_5–C_{13}	C_8, C_9, C_7, C_5, C_{10}	
polycrystalline graphite	C_5–C_{14}	C_7, C_6, C_9, C_{10}, C_{11}	C_{21}

Laser desorption of basal plane HOPG yielded abundant magic number cluster cations in the low-mass region (C_{11}^+, C_{15}^+, C_{19}^+, C_{23}^+) but no fullerene ions. This somewhat remarkable result appears to correlate with the minimal laser damage on HOPG samples compared to the other carbon solids. The visible absence of a macroscopic crater (channel) on HOPG may explain the lack of detectable C_{60}^+ formation: efficient fullerene production by means of direct laser desorption from graphite has been correlated with high laser power and the generation of a channel on the sample surface.[56]

The positive ion mass spectra of GC-6 and GC-25 both showed abundant low-mass magic number clusters (see Table I). The absence of fullerene cations upon laser desorption of GC-6 and GC-25 is not readily explained. One possibility is that it is difficult to attain a high-density laser plasma at the surface of glassy carbon since it is mechanically harder (and presumably more difficult to vaporize) than graphite. Recently, a lower macroscopic fullerene yield from the soot of arc-welded glassy carbon rods vs graphite rods (~1.3% vs ~12%) has been observed.[57] LD/MS of both GC-6 and GC-25 gave abundant ions from C_{14}^+ to C_{32}^+, although C_{29}^+ to C_{32}^+ were relatively more abundant for the GC-6 material. The minor differences in C_n^+ ion relative yields between GC-6 and GC-25 may be the result of larger graphitic crystallites for GC-25 than GC-6.

Carbon Electrode Solids: Negative Ions. Table II contains a summary of the carbon cluster negative ions observed for the various carbon solids. A consistent characteristic of the negative ion FT/ICR mass spectra of the four carbon materials is the presence of C_5^- to C_{13}^-. As seen in Figure 2 (right-hand spectra), the mass spectra of polycrystalline graphite and HOPG are very similar over the range $50 < m/z < 180$, with the exception of C_8^- at low apparent abundance for polycrystalline graphite (possibly an artifact of insufficient digital resolution). On occasion, laser desorption of basal plane HOPG yielded abundant C_{60}^- and C_{70}^- ions. Since the basal plane of HOPG is atomically flat,[1] we believe that HOPG efficiently reflected the focused high-power laser pulse onto the ICR trap electrodes, where residual carbon soot may have previously been deposited.

Negative ion laser desorption FT/ICR/MS of GC-6 revealed carbon cluster ions extending up to C_{17}^-, as well as C_{21}^- and C_{25}^- (see Figure 2). GC-6 also gave relatively

---

(54) Dreyfus, R. W.; Kelly, R.; Walkup, R. E. *Nucl. Instrum. Methods Phys. Res.* **1987**, *B23*, 557–561.

(55) Bloomfield, L. A.; Geusic, M. E.; Freeman, R. R.; Brown, W. L. *Chem. Phys. Lett.* **1985**, *121*, 33–37.

(56) O'Keefe, A.; Ross, M. M.; Baronavski, A. P. *Chem. Phys. Lett.* **1986**, *130*, 17–19.

(57) Coe, J. V., Unpublished results, 1992. The glassy carbon rods were GC-30, and the graphite rods were Ultracarbon UF-4S grade.

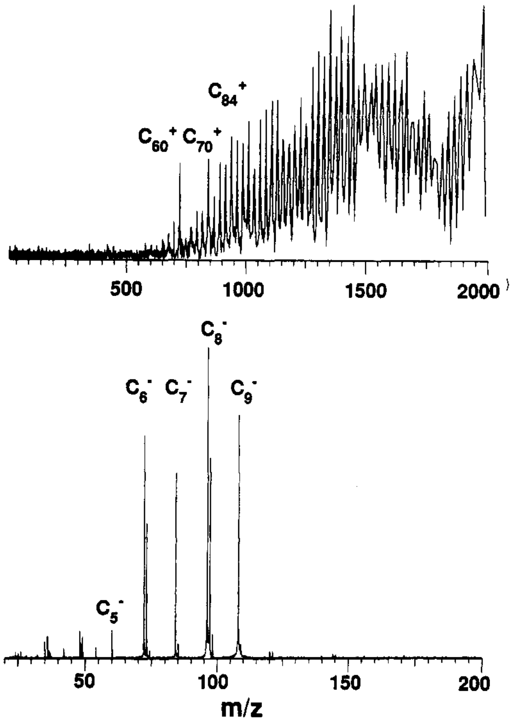

Figure 3. Positive and negative ion laser desorption mass spectra of poly(phenylenediacetylene) over the range $20 < m/z < 2000$ for positive ions and $20 < m/z < 200$ for negative ions. The more abundant carbon cluster ions, C_n^+ and C_n^-, are identified by their n values.

abundant C_nH^- ions for $n = 8, 10$, and 12. Abundant C_8H^-, $C_{10}H^-$, and $C_{12}H^-$ ions were also observed in the laser desorption FT/ICR mass spectrum of GC-6 doped with 1 atom % of platinum (not shown). Other investigators have previously noted abundant C_nH^- ions from laser desorption mass spectrometry of polycyclic aromatic hydrocarbons,[58] carbon films,[59] and carbon oxides.[22] The laser desorption FT/ICR negative ion mass spectra of GC-25 and GC-6 in the range C_5^- to C_{13}^- are quite similar.

Poly(phenylenediacetylene). For comparison, the laser desorption mass spectrum of poly(phenylenediacetylene), the organic precursor to GC-6, is shown in Figure 3. Since poly(phenylenediacetylene) is quite reactive, the laser power was reduced by a factor of ~100, time domain data were collected from individual laser shots, and the sample disk was degassed to a pressure of $\sim 6 \times 10^{-8}$ Torr prior to LD/MS. Repeated laser shots on the poly(phenylenediacetylene) changed the color of the disk from yellow to black near the laser spot. Fullerene ions from C_{60}^+ to at least C_{150}^+ were obtained in positive-ion mode. No significant signal was obtained for low-mass carbon cluster cations (C_5^+ to C_{30}^+). In contrast, *only* low-mass carbon cluster ions were obtained in negative-ion mode (C_3^- to C_{10}^-, principally C_6^- to C_9^-). Poly(phenylenediacetylene) also gave abundant C_6H^- and C_8H^- ions. The detection of fullerene cations from poly(phenylenediacetylene) is consistent with previous LD/MS of other organic precursors,[19-21] in support of the hypothesis that fullerene cations are readily formed by ion-molecule reactions, whereas fullerene anions are generated by a different mechanism (resonant electron attachment).

Conclusions

We have compared the Nd:YAG pulsed laser desorption FT/ICR positive and negative ion mass spectra of GC-6, GC-25, HOPG, and polycrystalline graphite under similar experimental conditions. Polycrystalline graphite is distinguished from the other three carbon materials in positive ion mode by the presence of fullerene ions from C_{44}^+ to C_{124}^+. All four carbon solids yielded abundant C_{11}^+, C_{15}^+, C_{19}^+, and C_{23}^+ ions. GC-6 gave somewhat more abundant C_{14}^- to C_{17}^-, $C_{10}H^-$, and $C_{12}H^-$ ions compared to the other carbon materials. The negative ion FT/ICR mass spectra of GC-25, HOPG, and polycrystalline graphite were qualitatively similar, exhibiting clusters from C_5^- to C_{13}^-. Laser desorption from a disk of poly(phenylenediacetylene) yielded fullerene cations, but only C_3^- to C_{10}^- carbon cluster anions. The differences in positive- and negative-ion mass spectra of carbon clusters suggest different ion formation mechanisms for these species.

Acknowledgment. We thank R. L. McCreery for many helpful discussions. We also thank D. Zavitz for assistance with the Raman spectroscopy of the carbon samples, and we thank A. Moore from Union Carbide for providing us with HOPG samples. This work was supported by NSF (CHE-9021058, CHE-9007132) and The Ohio State University.

---

(58) Balasanmugam, K.; Viswanadham, S.; Hercules, D. M. *Anal. Chem.* **1983**, *55*, 2424–2426.

(59) Siperko, L. M.; Brenna, J. T.; Creasy, W. R. *J. Vac. Sci. Technol.* **1990**, *A8*, 1533–1537.