Expansion Dynamics of Carbon Cluster Ions (C_n^+, n = 1-24) Produced by Laser Ablation of a Graphite Target

Chang Hyun Bae and Seung Min Park*

Department of Chemistry and Research Institute for Basic Sciences, Kyunghee University, Seoul 130-701, Korea
Received April 8, 2002

Key words : Carbon cluster, Laser ablation, Expansion dynamics

Laser ablation of graphite is unique in that carbon clusters of various sizes are created even in vacuum condition where condensation of atomic species cannot be expected to help growth of clusters as in the case of supersonic expansion. Carbon clusters are formed by irradiation of a graphite target as long as the atomic density is sufficiently high near the target surface and remain considerably stable, while metal clusters produced such are in general bound weakly and hardly survive high temperatures in the plume.[1]

Since the pioneering work of Berkowitz *et al.*,[2] numerous researchers have studied carbon clusters produced by laser ablation of graphite and concluded that neutral and ionic carbon clusters are generated at an early stage of laser ablation near the graphite surface.[3] By laser ablation of a graphite target, carbon clusters and their ions are formed by several mechanisms: direct ablation, chemical reaction in the gas phase, and dissociation of larger clusters. Among these, the dominant route of formation is determined mostly by experimental parameters like laser wavelength, fluence, background pressure, and surface morphology of a target. For example, the carbon plume produced at 266 nm consists mainly of C and C_3 due to efficient fragmentation while larger clusters are abundant at 1064 nm[4] and the craters on the graphite surface formed by prolonged laser irradiation are believed to be responsible for the formation of, in particular, large (n > 30) carbon clusters.[5-8]

The mass spectral carbon cluster distribution is strongly dependent not only on the experimental conditions but also on the sampling position in the laser-induced plasma plume. This is determined by either the timing of the high-voltage pulse applied to the electrodes in the time-of-flight (TOF) mass spectrometer for ionic clusters or the time-delay of the ionizing laser pulse for neutral clusters since the arrival time of carbon clusters at the sampling region is mass-dependent.

By adopting quadrupole mass spectrometer (QMS), however, we can obtain TOF spectra and *time-integrated* intensities of carbon clusters or their ions produced by laser ablation. More accurate analysis of expansion dynamics of carbon clusters is thus made possible by TOF quadrupole mass spectrometry (TOFQMS) although the mass range is limited by QMS. For small carbon clusters, C_n (n < 4) and their ions, C_n^+, formation mechanisms and energetics were examined previously[9,10] by using TOFQMS but studies on the expansion of the larger carbon clusters have not been reported. In this work, we present experimental results on the expansion mechanism of carbon cluster ions, C_n^+ ($1 \leq n \leq 24$) produced by laser ablation of graphite for the first time to our knowledge. Also, we have studied the effects of the ambient gas pressure in the ablation region.

The experimental setup has been described previously.[10] Briefly, the apparatus consists of a target chamber and an analysis chamber, which are separated by a skimmer with an orifice diameter of 0.97 mm. Laser ablation occurs in the target chamber, where a 20 mm diameter graphite target (Nilaco, 99.99%) is rotated by a standard rotary motion feedthrough to avoid a target aging effect. The 1064 nm radiation from a Nd:YAG laser (Continuum, Minilite II) is focused onto the target by using a 500 mm lens at an incident angle of 52°. The laser fluence is fixed at 0.57 J/cm^2 throughout the experiment.

The analysis chamber is equipped with a quadrupole mass spectrometer (VG SX300), whose resolution is approximately 1 amu. The flight distance of ions, 48 cm, is defined as the length between the target and an entrance hole to a detector. Ion optics in front of the quadrupole housing are grounded and the ionizer is turned off during the experiment to detect ions only. Three hundred laser shots are irradiated on the rotating target surface, each giving a TOF spectrum. These spectra are averaged into a single TOF spectrum by a storage oscilloscope (LeCroy 9361, 300 MHz). The typical equilibrium pressures of the target and the analysis chamber with the laser impinging the are 6.7×10^{-7} Torr and 1.9×10^{-7} Torr, respectively.

TOF spectra of C_n^+ (n = 1, 3, 11, 18) ions are shown in Figure 1. C^+ ions have narrow time-of-arrival or velocity distribution indicating that they are formed at the early stage of plume formation or by direct ejection from the graphite surface. C_3^+ is the major fragment ion produced in the plume by either collision-induced dissociation or photodissociation and thus shows a long tail. The TOF distributions of C_{11}^+ and C_{18}^+ ions are quite broadened since they are produced mainly by fragmentation of larger clusters and their scattering cross sections in the plume are relatively large. In particular, C_{11}^+ ions show a clear bimodal distribution, which indicates collision-induced dissociation of larger cluster ions. Such bimodal distribution is not clearly observed for other ions presumably because the velocity distributions are narrow or the signal-to-noise ratios are low.

The distribution of cluster ions is determined at an early stage of laser ablation, where the diameter of the plume is at

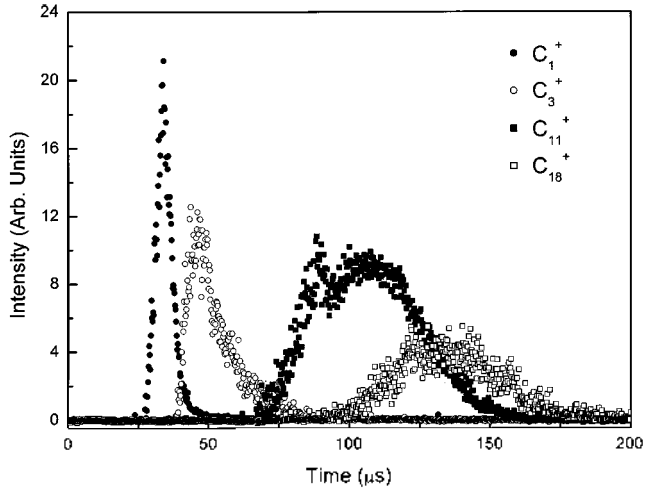

Figure 1. The time-of-flight spectra of C_n^+ (n = 1, 3, 11, 18) ions formed by laser ablation of a graphite target in high vacuum. The laser fluence was 0.57 J/cm^2.

most few mm. Since most ions are produced in the tiny plume, we may assume that the flight distance is the length between the target surface and the detector. Therefore, by analyzing the TOF distributions, we can obtain the mean velocities and mean kinetic energies of C_n^+ (n = 1-24) ions as depicted in Figure 2. The mean velocity ranged from 14.5 km/s (C^+) to 3.3 km/s (C_{21}^+) and decreased monotonously with increasing cluster mass. The mean kinetic energies of C_n^+ ions are estimated to be about 15 eV regardless of the cluster size. The inset in Figure 2 shows a linear dependence of the mean velocity on $1/\sqrt{M}$, where M is the molecular mass. This implies that the expansion of C_n^+ ions is governed by the Coulomb attraction between the ions and the electrons escaping at the plume boundary. When the transient electric field in the plume plays a dominant role in the acceleration of ions, the velocities of ions are proportional to $1/\sqrt{M}$.[11] However, the reason why the mean kinetic energy of C^+ ions is smaller and that of C_3^+ ions is larger than those of other ions is not clear yet. Since the laser-produced carbon plume is a complicated system, the expansion of each ion is expected to be influenced by reactive and nonreactive scatterings in the plume as well as the local electric field.

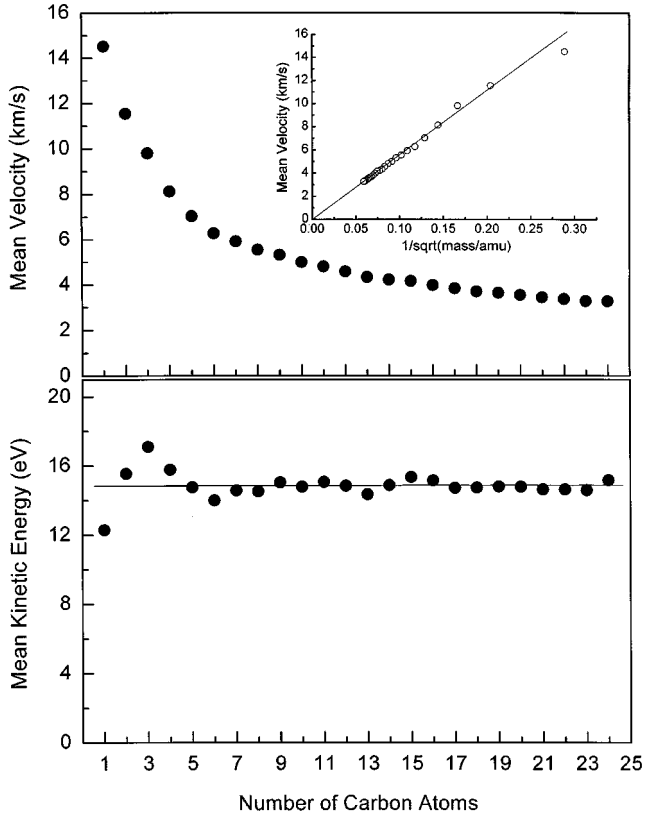

Figure 2. The mean velocities and mean kinetic energies of C_n^+ (n = 1-24) ions. The inset shows the linear dependence of the mean velocity on $1/\sqrt{M}$.

In order to examine the formation and expansion mechanisms of carbon cluster ions in an inert gas atmosphere, the signal magnitudes and mean velocities of the cluster ions were obtained as shown in Figure 3. The intensity of C^+ ions decreased with increase of Ar pressure most significantly. In an Ar atmosphere, the ablated species are scattered by Ar atoms to deviate from the target surface normal direction.[12] The deviation is more apparent for the lighter species since the scattering angle is in essence determined by the mass ratio of the ablated species and Ar atoms. The intensity of C_3^+ ions decreased less than that of C_{11}^+ ions since C_3^+ ions are the major fragment due to collision. The mean velocities of C_n^+ ions directed the target surface normal were unaltered as the ambient gas pressure was varied, which implies that

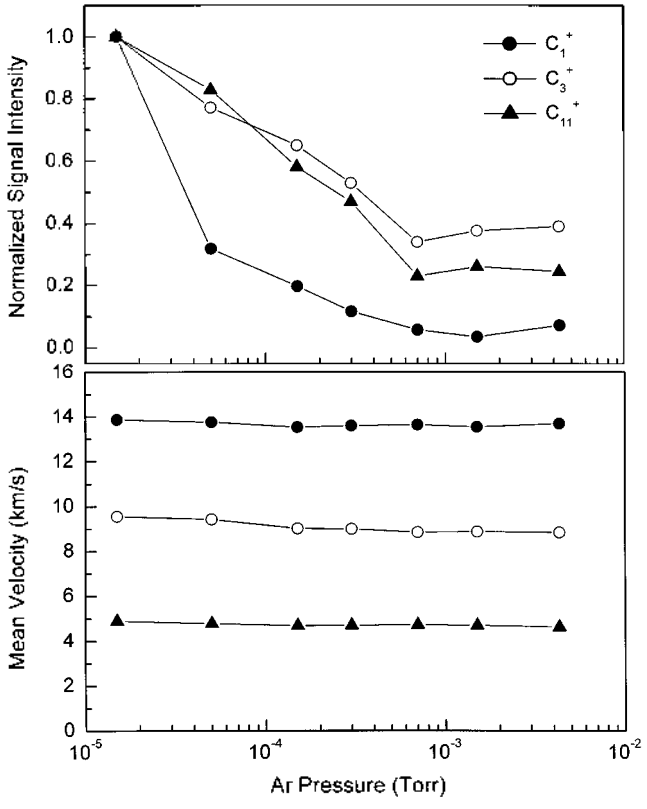

Figure 3. The normalized signal intensities and mean velocities of C_n^+ (n = 1, 3, 11) ions *vs.* Ar pressure.

the expansion of ions in the given pressure range is mostly determined by the local and temporal electric field in the plume formed by a charge separation.

In conclusion, we have demonstrated a linear dependence of the mean velocity of carbon cluster ions on $1/\sqrt{M}$ by using TOFQMS. Our results clearly shows that the kinetic energies of C_n^+ ions in the carbon plume are determined by a nonthermal phenomena like a local and temporal electric field formed by a charge separation in the plume[13] and the laser ablation of graphite may not be considered to be a simple thermally activated vaporization process.[14] High kinetic energies of *neutral* carbon atoms and small carbon molecules,[15] which cannot be explained by thermal aspects of laser ablation, may stem from charge-exchange collisions between fast ions and neutrals.

Acknowledgment. This work was supported by grant No. R01-2000-00040-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

References

1. Rohlfing, E. A.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* **1984**, *81*, 3322.
2. Berkowitz, J.; Chupka, W. *J. Chem. Phys.* **1964**, *40*, 2735.
3. Radi, P. P.; Bunn, T. L.; Kemper, P. R.; Molchan, M. E.; Bowers, M. T. *J. Chem. Phys.* **1988**, *88*, 2809.
4. Gaumet, J. J.; Wakisaka, A.; Shimizu, Y.; Tamori, Y. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 1667.
5. O'Keefe, A.; Ross, M. M.; Baronavski, A. P. *Chem. Phys. Lett.* **1986**, *130*, 17.
6. McElvany, S. W.; Creasy, W. R.; O'Keefe, A. *J. Chem. Phys.* **1986**, *85*, 632.
7. Pradel, P.; Monchicourt, P.; Laucagne, J. J.; Perdrix, M.; Watel, G. *Chem. Phys. Lett.* **1989**, *158*, 412.
8. Togashi, H.; Saito, K.; Koga, Y.; Yamawaki, H.; Aoki, K.; Mukaida, M.; Kameyama, T. *Appl. Surf. Sci.* **1996**, *96-98*, 267.
9. Park, S. M.; Moon, J. Y. *J. Chem. Phys.* **1998**, *109*, 8124.
10. Park, S. M.; Chae, H.; Wee, S.; Lee, I. *J. Chem. Phys.* **1998**, *109*, 928.
11. Marine, W.; Gerri, M.; Scotto d'Aniello, J. M.; Sentis, M.; Delaporte, Ph.; Forestier, B.; Fontaine, B. *Appl. Surf. Sci.* **1992**, *54*, 264.
12. Chen, X. Y.; Xiong, S. B.; Sha, Z. S.; Liu, Z. G. *Appl. Surf. Sci.* **1997**, *115*, 279.
13. Chrisey, D. B.; Hubler, G. K. *Pulsed Laser Deposition*; Wiley: New York, U. S. A., 1994; p 118.
14. Dreyfus, R. W.; Kelly, R.; Walkup, R. E. *Nucl. Instrum. Meth. Phys. Res. B* **1987**, *23*, 557.
15. Krajnovich, D. J. *J. Chem. Phys.* **1995**, *102*, 726.