computational proteomics

Laboratory for Computational Proteomics

www.FenyoLab.org

E-mail: Info@FenyoLab.org

Facebook: *NYUMC Computational Proteomics Laboratory*

Twitter: *@CompProteomics*

Formation of fullerenes in MeV ion track plasmas

Gunnar Brinkmalm [a], Douglas Barofsky [b], Plamen Demirev [a], David Fenyö [a], Per Håkansson [a], Robert E. Johnson [c], Curt T. Reimann [a] and Bo U.R. Sundqvist [a,1]

[a] *Division of Ion Physics, Department of Radiation Sciences, Uppsala University, Box 535, S-75121 Uppsala, Sweden*

[b] *Department of Agricultural Chemistry, Oregon State University, Corvallis, OR 99331-6502, USA*

[c] *Department of Nuclear Engineering and Engineering Physics, University of Virginia, Charlottesville, VA 92901, USA*

Received 28 October 1991; in final form 18 December 1991

MeV primary $^{127}I^{14+}$ ions from the Uppsala EN-tandem accelerator were used to bombard a polymer – poly(vinylidene difluoride). Positive ions of even numbered carbon clusters (C_n^+, $n=40$–120) are ejected as a result of the interaction of fast MeV ions with the organic solid. The distribution of cluster sizes suggests that stable, closed carbon-cage structures – fullerenes – are formed. Initial radial velocity distributions of the desorbed carbon species are consistent with preferential ejection backward into the direction of the incoming MeV ions. Correlation between the directions of incoming particles and ejected clusters suggests that the latter (including C_{50}^+ and C_{60}^+) originate in the infratrack plasma produced by the fast primary ion's interaction with the sample. A main conclusion resulting from this study is that carbon cluster ions form as a result of a single primary ion impact and that they are ejected from an axially expanding infratrack plasma region.

1. Introduction

In a secondary ion mass spectrometry (SIMS) experiment on poly(vinylidene difluoride) (PVDF) with ^{252}Cf fission fragments with energy of 1 MeV/ n, Feld et al. [1] have observed positive ions of even numbered carbon clusters. Rohlfing et al. [2] were the first to report formation of large carbon clusters by laser evaporation of graphite followed by cooling in a supersonic molecular beam. Subsequently Kroto et al. [3] in a similar type of experiment found conditions for enhancing the yield of C_{60}^+. Its stability was associated with the "uniquely elegant" structure of a truncated icosahedron that was given the name (buckminster) fullerene [3]. Kroto has extended the term "fullerene" to denote all even number carbon clusters with closed carbon cages [4]. Recently a method was devised by Krätschmer et al. [5] for the preparation of macroscopic amounts of C_{60} and C_{70} fullerenes.

One of the original motives for studying fullerenes resulted from interest in elucidating carbon-star chemistry [4]. Different mechanisms of carbon cluster formation by laser evaporation from either graphite or synthetic polymers have been discussed [6–10]. Kroto has proposed the "icospiral particle nucleation scheme" [4]. According to that model, fullerene formation, which occurs in the expanding He jet, takes 10^{-4} s to complete. Moreover, almost all investigators using lasers for direct formation of carbon clusters (without employing gas jet cooling) stress the importance of factors, such as long laser irradiation times, which produce macroscopic channels in the target [7–9], and direction of magnetic field in ion cyclotron resonance measurements [8]. All these factors facilitate ion/molecule reactions in the expanding plume, but limit any estimate of fullerene formation to at least 100 ns. In this Letter, evidence is presented that fullerenes might be formed orders of magnitude more rapidly in infratrack plasmas formed by fast MeV ions, which may have implications on understanding fullerene formation under different conditions including those present in stellar environments.

---

[1] To whom correspondence should be addressed.

2. Experimental

Fast ions (72.3 MeV $^{127}I^{14+}$) from the EN-tandem accelerator of the "The Svedberg Laboratory" (Uppsala) have been used to bombard films of PVDF polymer, $(-CH_2-CF_2-)_n$, at a 45° incidence angle (see inset of fig. 1). The primary beam intensity was around 2000 particles per second on a sample area of 2 mm², while the total dose was 10^6 primary ions. This static bombardment mode ensured that each primary particle interacts with locally undamaged polymer sample. PVDF films 100 nm thick were deposited on stainless steel backings by spin coating an acetone solution of the polymer. The secondary ions produced were mass analyzed in a time-of-flight mass spectrometer fitted with a 180° ion mirror [11]. The instrument has a maximum resolution of 10500 ($M/\Delta M$ at fwhm). A static electric field of +15 kV applied to the target was used to extract and accelerate the ejected secondary ions through a grid at ground potential into the first field free drift region. The data were acquired in an event by event mode with single ion counting. A multistop time to digital converter with a resolution of 0.5 ns per channel was employed for that purpose. Two pairs of deflection plates are placed before the first field-free region of the spectrometer. The initial ra-

dial velocity distributions of the secondary ions were determined, as described elsewhere [12,13], by measuring the yield of a particular secondary ion as a function of voltage applied to the deflection plates.

3. Results and discussion

Fast ion–solid interactions occur on scales shorter than 10^{-12} s, i.e. at least four orders of magnitude faster than nanosecond laser ablation/desorption. There are also other major differences between these two entirely different means of excitation of the solid; some are listed briefly for clarity reasons. Most of the energy of MeV ions (whose velocities exceed the Bohr velocity) is deposited in a solid target via ion-electron collisions in an ion track. The track is axially symmetric along the direction of the incoming ion. Plasma-like conditions are formed in an infra-track, a cylindrical region roughly 5 Å in radius where the energy density is greatest. On the contrary the excited area in laser ablation has a diameter of the order of μm, i.e. the laser beam spot size. Thus the excited surface is macroscopic for laser ablation and microscopic for MeV ion–solid interactions. Consequently the amount of ejected material is also several orders of magnitude larger (plume formation)
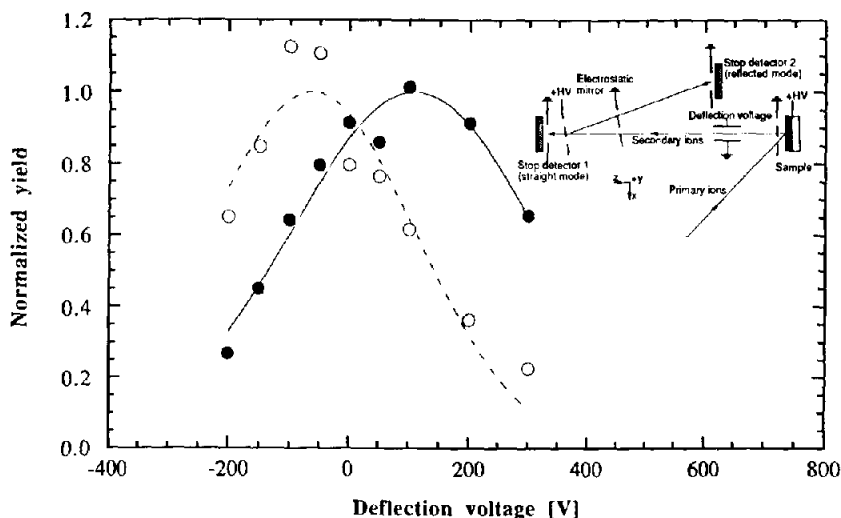

Fig. 1. Yield of $C_2H_3^+$ ions (closed circles) and molecular ions (MH$^+$) of a peptide-renin substrate (mass 1802 u, open circles) desorbed from a thin sample layer as a function of the voltage between the deflection plates in the x direction. The data points have been fitted to Gaussian curves. The inset is a schematic of the experimental setup (the y direction deflection plates have been omitted in the figure).

in the laser ablation case. The lifetime of the MeV ion infratrack plasma is of the order of 10^{-13} s and this region is believed to consist mainly of positive ions prior to neutralization. If the electronic relaxation in the solid is slow, as in the case of insulators, material is sputtered from the solid. This phenomenon is termed electronic sputtering, and it has important astrophysical implications [14]. Electronic sputtering is also exploited in a specific version of SIMS – plasma desorption mass spectrometry (PDMS) – for studies of biological macromolecules with molecular weights up to 45 kDa [15,16]. The mechanism of the electronic sputtering phenomenon has been studied quite extensively [17,18]. The currently accepted model assumes that a pressure pulse (shock wave) propagates radially from the track core as a result of the large energy gradients. The pressure pulse leads to a directed momentum transfer and ejection of multiatomic systems, including large intact biomolecules [18], from the ultratrack – a region of lower energy density further away from the ion track core. The analytical pressure pulse model [17] has been shown to be consistent with the results of molecular dynamics simulations [19]. An important confirmation of the pressure pulse model is the correlation between the directions of incoming ions and ejected molecular ions of large labile biomolecules. According to the model, these ions are ejected preferentially in a direction away from that of the incoming ion as a result of the pressure pulse propagating outward, radially to the ion track [12,13] (fig. 1). This effect, which is manifested in nonsymmetrical, initial radial velocity distributions of desorbed peptide molecular ions, has been experimentally verified [12,13] and has also been simulated by computer [19]. These shifted distributions observed for different biomolecules should be contrasted with the ejection of lower mass ions (e.g. alkali metal ions or fragments like CH_3^+ and $C_2H_3^+$) that have ejection angular distributions symmetric about the surface normal.

In the present experiment, positive secondary ions emitted from PVDF were studied. The ion peaks of the large even numbered carbon clusters with clearly resolved isotope peaks (C_n, $n = 40$–120) are shown in fig. 2. Clusters with not clearly resolved isotope peaks but separated by 24 u mass difference are extending up to m/z 4000. These spectra are obtained
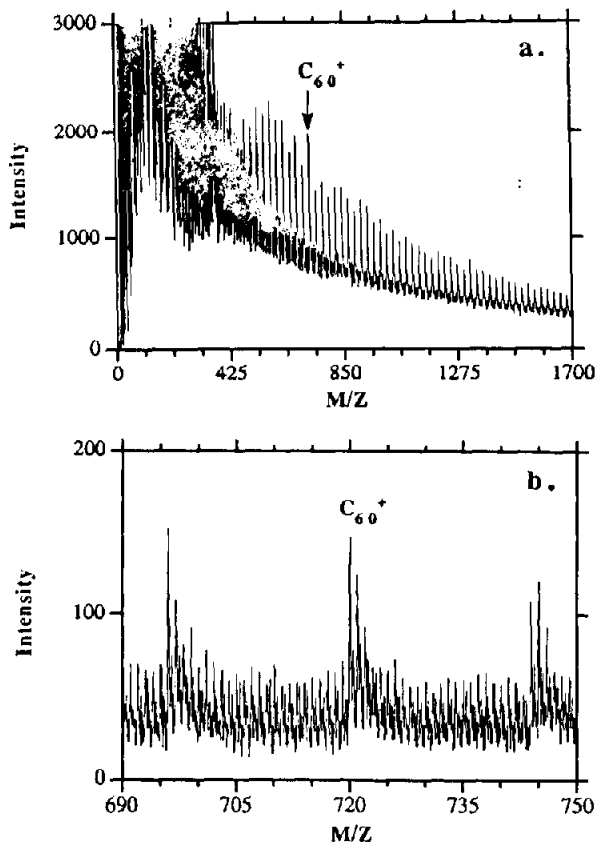

Fig. 2. (a) Positive ion mass spectrum obtained from PVDF in the range 0–1700 m/z. Even numbered carbon cluster ions (C_n, $n = 40$–138) are clearly observed. (b) Expanded view of the region m/z 690–750 from the same spectrum.

during static MeV-ion bombardment, clearly indicating that carbon clusters are produced in a single MeV-ion impact. The integrated yield (number of secondary ions per incident primary ion) of these large cluster ions is about 1. There is, consequently, no ion-induced macroscopic carbonization of the sample surface preceding the ejection of carbon clusters as suggested previously [1]. Carbonization of the polymer is not a prerequisite for carbon cluster emission under MeV ion impact, which is also illustrated by the fact that total sputtering yields from graphite (a conductor) when bombarded by MeV ions are negligible.

The change in isotopic distribution of the secondary ions (C_n, $n = 40$–120) as well as accurate determination of their mass shows that pure carbon clus-

347

ters are detected (by contrast no pure carbon clusters were observed when teflon $(-CF_2-CF_2-)_n$ was bombarded under the same experimental conditions). There is also a peak at every integer mass in the PVDF spectrum indicating that, as expected, many combinations of hydrogenated carbon clusters are produced as well. We were not able to find any mixed fluorohydrocarbon ions in the spectrum. In fig. 3 the yield of carbon cluster ions from PVDF is shown as a function of number of atoms in the cluster. The intensity modulation suggests that C_{50} and C_{60} are indeed more stable than the others. This fact as well as the observation of only even numbered carbon species strongly indicates that fullerenes are formed [3,4,6] in the process. This conclusion cannot be directly confirmed since there are no straightforward methods available at present for probing the structure of gas phase ions.

The initial radial velocity distribution of the ejected carbon cluster ions from PVDF was studied. Deflection data for the fragment ion, $C_2H_3^+$, which is emitted mainly along the normal to the sample surface [12,13] (and thus used as a reference), are shown together with the results for the C_{60} cluster ions from PVDF (fig. 4). The unusual finding is that carbon cluster ions are ejected preferentially backwards along the direction of the ion track in a "jet effect" (we use this term without any implications of plume formation as in e.g. laser ablation). To our knowledge, this is the first time such a process has been observed in sputtering. The "jet effect" is also observed with the other large carbon clusters and the F^+ ion, emitted from the PVDF sample. This result is in direct contrast to the ejection angle distributions for the molecular ions of the large organics discussed above. The results of the present study imply that carbon clusters observed in MeV particle bombardment of PVDF polymer (containing only 30% carbon atoms) originate in the infratrack region at high energy densities and that furthermore these clusters (or their precursors) are ejected by axial expansion of the track core, which would account for the observed "jet effect". Such a mechanism is obviously quite different from the desorption mechanism for the labile molecular ions of, for example, peptides ejected from the ultratrack by a radially propagating pressure pulse. It also seems most likely that hydrogen and fluorine rapidly form hydrogen fluoride – a necessary prerequisite for formation of the large even carbon cluster ions from PVDF since clusters were not observed in the case of teflon. Based on the observed peak shapes, which are nearly symmetric, one may rule out a hypothesis that the carbon clusters are decay products of a fullerene precursor (a "hot" piece of the polymer, enriched in C) that cools down by evaporation in the accelerating region of the spectrometer. However, the resolution of the time to digital converter used (0.5 ns/channel) gives a lower limit for such a process. On the other hand changing the total flight time (in the mi-
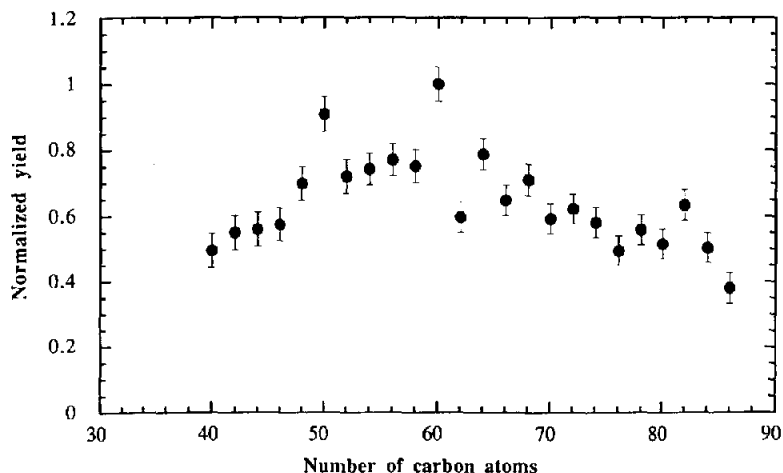

Fig. 3. Yield of carbon cluster ions (C_n, $n=40$–86) desorbed from a PVDF sample as a function of number of atoms in the cluster.
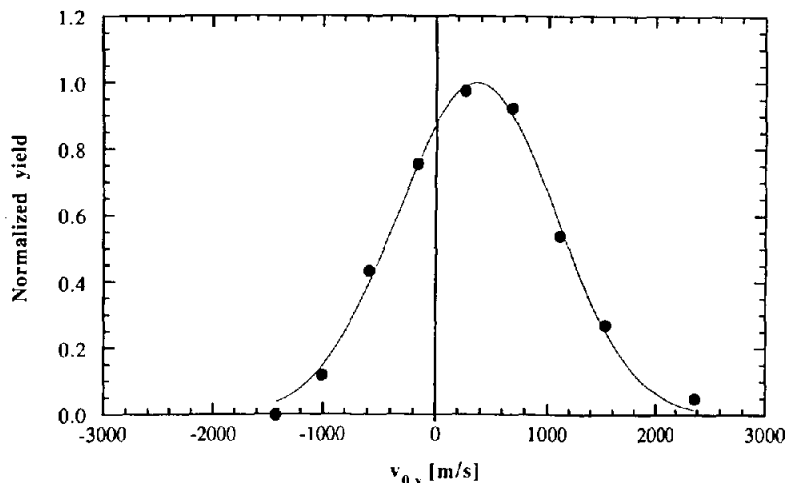
Fig. 4. Initial radial velocity distribution of C_{60}^+ ions desorbed from a PVDF sample. The distribution is relative to the distribution of $C_2H_3^+$ ions which are desorbed symmetrically around the normal to the sample surface. The data points have been fitted to a Gaussian curve.

crosecond time scale) of different cluster ions through the system by changing the acceleration voltage has a negligible effect on both the relative intensity distribution of the different clusters and their relative peak shapes. These observations indicate that all decomposition and rearrangement reactions (if any) for the observed carbon cluster ions are completed in a nanosecond or less before they are accelerated to the full energy at which they are transported through the flight tube of the mass analyzer.

The main conclusion from this study concerns the primary ion dose and the time scale for formation of the observed carbon clusters. We have demonstrated that fullerenes can be produced in electronic sputtering from PVDF in a single ion impact. The preferentially non-normal ejection of carbon clusters back along the direction of the incoming primary ion strongly suggests that they are formed at very high energy densities in the infratrack plasma and ejected by the axially expanding track core. This finding may bear implications for the mechanism of fullerene formation in general. From molecular dynamics simulations of electronic sputtering of organic solids [19], one can deduce the time scale for expansion of the infratrack and estimate an ejection time for a carbon cluster or its precursor to be of the order of 10^{-12} s. Assuming that the observed cluster ions are formed as a result of cooling off by decay and rear-

rangement of precursors ejected in this picosecond time domain, a very conservative upper limit of one nanosecond has been estimated for the time of fullerene formation. Hence, we are led to the conclusion that in the ion track plasma region of a single primary ion fullerenes are created on a time scale of 10^{-12}–10^{-9} s, i.e. in a time at least five orders of magnitude shorter than previously suggested [4].

Acknowledgement

References

[1] H. Feld, R. Zurmühlen, A. Leute and A. Benninghoven, J. Phys. Chem. 94 (1990) 4595.

[2] E.A. Rohlfing, D.M. Cox and A. Kaldor, J. Chem. Phys. 81 (1984) 3322.

[3] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley, Nature 318 (1985) 162.

[4] H. Kroto, Science 242 (1988) 1139.

[5] W. Krätschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, Science 347 (1990) 354.

[6] S.C. O'Brien, J.R. Heath, R.F. Curl and R.E. Smalley, J. Chem. Phys. 88 (1988) 220.

[7] P.P. Radi, M.T. Hsu, J.M. Brodbelt-Lustig, M. Rincon and M.T. Bowers, J. Chem. Phys. 92 (1990) 4817.

[8] S.W. McElvany, H.H. Nelson, A.P. Baronavski, C.H. Watson and J.R. Eyler, Chem. Phys. Letters 134 (1987) 214.

[9] E.E. Campbell, G. Ulmer, B. Hasselberger, H.-G. Busmann and I.V. Hertel, J. Chem. Phys. 93 (1990) 6900.

[10] W.R. Creasy and J.T. Brenna, J. Chem. Phys. 92 (1990) 2269.

[11] G. Brinkmalm, P. Håkansson, J. Kjellberg, B.U.R. Sundqvist, P. Demirev and W. Ens, Intern. J. Mass Spectrom. Ion Processes, submitted for publication.

[12] W. Ens, B.U.R. Sundqvist, P. Håkansson, A. Hedin and G. Jonsson, Phys. Rev. B 39 (1989) 763.

[13] D. Fenyö, A. Hedin, P. Håkansson and B.U.R. Sundqvist, Intern. J. Mass. Spectrom. Ion Processes 100 (1990) 63.

[14] R.E. Johnson, Energetic charged-particle interactions with atmospheres and surfaces (Springer, Berlin, 1990).

[15] B.U.R. Sundqvist, Nucl. Instr. Meth. B 48 (1990) 517.

[16] K. Wien, Rad. Eff. Def. in Solids 109 (1989) 137.

[17] R.E. Johnson, Intern. J. Mass Spectrom. Ion Processes 78 (1987) 357.

[18] R.E. Johnson, B.U.R. Sundqvist, A. Hedin and D. Fenyö, Phys. Rev. B 40 (1989) 49.

[19] D. Fenyö, B.U.R. Sundqvist, B. Karlsson and R.E. Johnson, Phys. Rev. B 42 (1990) 1895.