NEGATIVE CARBON CLUSTER ION BEAMS: NEW EVIDENCE FOR THE SPECIAL NATURE OF C_{60}

Y. LIU, S.C. O'BRIEN [1], Q. ZHANG, J.R. HEATH [1],
F.K. TITTEL, R.F. CURL, H.W. KROTO [2] and R.E. SMALLEY
Rice Quantum Institute and Departments of Chemistry and Electrical Engineering,
Rice University, Houston, TX 77251, USA

Received 28 March 1986

Cold carbon cluster negative ions are formed by supersonic expansion of a plasma created at the nozzle of a supersonic cluster beam source by an excimer laser pulse. The observed distribution of mass peaks for the C_n^- ions for $n > 40$ demonstrates that the evidence previously given for the special stability of neutral C_{60} and the existence of spheroidal carbon shells cannot be an artifact of the ionization conditions.

1. Introduction

In previous papers [1–3] on the vaporization products of graphite, we have presented evidence for formation of a remarkably stable C_{60} (buckminsterfullerene) molecule and proposed, as an explanation for this stability, that it has the highly symmetric truncated icosahedron structure. In this report, we describe the preparation of the jet-cooled negative ion of this and other carbon clusters, and observations which further demonstrate the special nature of C_{60} and the special stability of even (versus odd) carbon clusters in the size range of 40–80 atoms.

2. Experimental

The apparatus and technique for producing cold negative cluster ions have been described in previous publications [4,5] from this laboratory. In brief, carbon is vaporized from the surface of a rotating graphite disk by the second harmonic of a *Q*-switched Nd:YAG laser and entrained in a pulse of He carrier gas flowing down a 2 mm diameter tube. The 2 mm tube is expanded into a 4 mm tube 2 cm long with a lipped end (integrating cup) opening into a large vacuum chamber. An excimer laser pulse (KrF 248 nm) crosses the gas flow at this point producing negative cluster ions. The gas stream then completes its supersonic expansion producing a molecular jet containing very cold negative (and positive) ions as well as neutrals. The jet is skimmed into a molecular beam, and after a free flight of approximately 60 cm, the beam enters a deflection region where negative ions are stripped out by a voltage pulse on a pair of deflection plates. The negative ions are then mass-analyzed by flight time so that the distribution of the cluster ions produced can be examined.

3. Observations and results

Fig. 1a shows the negative cluster ion distribution near C_{60} as observed by time-of-flight mass spectrometry. Under these conditions C_{60}^- is clearly the dominant mass peak in this region. The relative peak heights of the negative ion cluster distribution near C_{60}^- is essentially independent of laser fluence over

---

[1] Robert A. Welch Foundation Predoctoral Fellow.

[2] School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK.

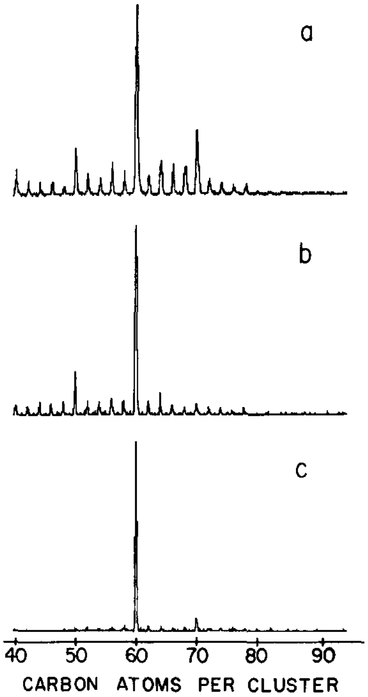

Fig. 1. Distribution of negative and positive carbon cluster ions of cluster size between 46 and 74 atoms. (a) depicts the distribution of negative cluster ions formed when the cluster pulse is intercepted just in front of the 4 mm expansion tube by KrF excimer laser (248 nm) radiation (fluence ≈1 mJ/cm^2). In (b) the distribution of positive ions produced by F_2 laser (157 nm) ionization in the source of the time-of-flight mass spectrometer 1 m downstream is shown. (c) shows the positive ion distribution produced by ArF excimer laser (193 nm) photoionization in the molecular beam at the same point downstream.

the range 0.01 to 1 mJ/cm^2 [‡] and is also not dependent upon whether KrF (248 nm) or ArF (193 nm) radiation is used.

The contrast ratio between the C_{60}^- peak and its near neighbors in fig. 1a is very similar to that observed (fig. 1b) when the neutral cluster beam produced under the same conditions (except for KrF laser pulse) is ionized by a F_2 laser pulse (157 nm) in the source chamber of a time-of-flight mass spectrometer located 1 m downstream. In contrast, as reported by Bloomfield et al. [6], the low mass intensity distribution of the negative ions is quite different from the positive ion distribution observed with downstream ionization.

Fig. 1c shows the positive ion spectrum reported previously [1] for the same vaporization and flow conditions using ArF (193 nm) ionization in the time-of-flight spectrometer source downstream. C_{60} and its near neighbors in size are all two-photon ionized by the ArF laser but appear to be one-photon ionized by the F_2 laser. We believe that the even greater contrast ratio of the C_{60} peak to other nearby peaks in fig. 1c versus 1a and 1b reflects great stability of C_{60} and C_{60}^+ to photofragmentation. Note finally that in all three ion distributions shown in fig. 1 only *even* cluster ions are present for clusters of size above 40.

Positive and negative cluster ions of carbon formed by laser vaporization were observed previously by Bloomfield et al. [6]. They observed that both even and odd C_n^- clusters are present for $n > 30$ with the odd clusters having approximately two-thirds the intensity of the even ones. Their observations on negative clusters did not extend to $n = 60$. For the positive ions formed in this manner, their observations show no difference in intensity between the even and odd clusters larger than 30 atoms except for n above 56. C_{60}^+ is the last ion clearly detected (their fig. 2b), and does not appear to be special. We are in complete agreement with their observations *on ions formed by laser vaporization*. However for *ionization downstream of the integrating cup*, the even clusters, and C_{60} in particular, are always dominant regardless of whether positive or negative ions are probed.

4. Discussion

The differences between the ion distribution produced by laser vaporization and that produced by downstream ionization can be very simply explained by noting that different chemical processes are taking place in the flow tube in the two cases. The *ion* distribution in laser vaporization should be determined by

---

[‡] There are very interesting changes in the ratio of low mass ($n < 20$) to high mass ($n > 27$) negative ion signals with laser fluence. At the lowest fluences used, while there are good signals from even clusters for $n = 28$ through $n = 70$, only very small signals are observed below $n = 28$ for KrF or ArF ionization. On the other hand, at the highest fluences with either laser, cluster ions with $n < 20$ are much more abundant than those with $n > 27$ (by roughly a factor of 30 with the ArF laser at ≈1 mJ/cm^2).

electron recombination and by charge exchange between clusters. We expect these ion processes to vary only slowly with cluster size and to be insensitive to the special nature of C_{60}. On the other hand as discussed previously [3], we believe that the *neutral* cluster distribution is determined by the relative resistance of the various clusters to chemical attack by small carbon species such as C_2 and C_3. The resistance to chemical attack of even clusters with $n > 40$ and C_{60} in particular can be most readily explained by these clusters having spheroidal carbon shell structures [3].

Thus C_{60} and other even neutral clusters of similar size which we detect appear to be *survivors* of the processes taking place before expansion with C_{60} being the most inert. The fact that the negative ion distribution produced by ionization in front of the flight tube is so similar to the positive ion distribution produced by laser photoionization of the beam a meter downstream is convincing evidence that the distributions shown in figs. 1a and 1b reflect the neutral cluster distribution and are *not* an artifact of the ionization process. This neutral distribution, in turn, is strong evidence supporting the spheroidal carbon shell model for even carbon clusters in this size range in general and the truncated icosahedron (soccer ball) model for C_{60} in particular.

Acknowledgement

This research was supported by the National Science Foundation and the Robert A. Welch Foundation, and used a laser and molecular beam apparatus supported by the US Army Research Office and the US Department of Energy. HWK thanks the SERC (UK) for travel assistance.

References

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

[2] J.R. Heath, S.C. O'Brien, Q. Zhang, Y. Liu, R.F. Curl, H.W. Kroto, F.K. Tittel and R.E. Smalley, J. Am. Chem. Soc. 107 (1985) 7779.

[3] Q. Zhang, S.C. O'Brien, J.R. Heath, Y. Liu, R.F. Curl, H.W. Kroto and R.E. Smalley, J. Phys. Chem. 90 (1986) 528.

[4] P.J. Brucat, L.S. Zheng, C.L. Pettiette, S.H. Yang and R.E. Smalley, J. Chem. Phys., to be published.

[5] L.S. Zheng, C.N. Karner, P.J. Brucat, S.H. Yang, C.L. Pettiette, M.J. Craycraft and R.E. Smalley, J. Chem. Phys., to be published.

[6] L.A. Bloomfield, M.E. Geusic, R.R. Freeman and W.L. Brown, Chem. Phys. Letters 121 (1985) 33.