

## Observation of “Stick” and “Handle” Intermediates along the Fullerene Road

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The hypothesis that fullerenes grow in a carbon plasma by the addition of C<sub>2</sub> units (the “fullerene road”) has been widely acclaimed as the most plausible mechanism for formation of larger fullerenes including C<sub>60</sub> and C<sub>70</sub>. Calculations suggest that the association of C<sub>2</sub> with fullerenes proceeds through two classes of intermediates, “sticks” and “handles.” Here we report the observation of these species using high-resolution ion-mobility measurements for C<sub>n</sub> cations generated by laser vaporization of graphite and laser desorption of C<sub>60</sub>. Sticks with up to eight-atom chains have also been found.

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Since the discovery that soccer-ball-like carbon molecules form upon vaporization of graphite [1,2], there has been tremendous interest in the mechanism of this extraordinary process. How the self-assembly of specific, perfectly symmetric fullerene cages occurs in substantial yield under the highly entropic conditions of a hot carbon plasma has been regarded as a major puzzle [3,4]. In the earliest “pentagon road” construct [5–9] fullerenes were envisioned to result from icospiral curling of graphite sheets that added pentagons along their edges during growth. A key role in this scenario is played by “cups” or “bowls” to which C<sub>2</sub> and other small carbon fragments add until the cage closes. However, these precursors have not been found for either cations or anions in the high-temperature carbon plumes where fullerenes are born [10–13]. This has been recognized as a critical flaw in the pentagon road hypothesis [4], and other inconsistencies in it have been pointed out elsewhere [14].

Later a different mechanism known as the “fullerene road” was proposed [15]. In this model, fullerenes release cage strain by inflating via sequential incorporation of C<sub>2</sub> units (and possibly other small carbon fragments) in the wall. This proposition has two strong advantages. First, it involves precursors (small fullerenes) that are in fact present in large abundance unlike the speculative cups [4]. Second, those precursors are low energy isomers, while the cups are quite high in energy compared even with graphite sheets [16]. Further, fullerenes dissociate by ejecting C<sub>2</sub> and shrinking regardless of the excitation method [17]. Of course, the above model does not tell the origin of small fullerenes. This issue has been addressed in the injected drift tube experiments, in which one can collisionally anneal ions at a controlled energy [10,18–20]. These studies have demonstrated efficient fullerene synthesis by isomerization of polycyclic carbon rings over a fairly low activation barrier. The same conclusion was reached from

other experiments [21], where fullerenes were produced by laser desorption of *cyclo*-C<sub>30</sub>(CO)<sub>10</sub> and its homologs. The problem here is that the prominence of particular fullerenes like C<sub>60</sub> or C<sub>70</sub> cannot easily be explained, because all the original rings are roughly equally abundant and should have similar reactivities [3]. However, magic sizes naturally ensue from the fullerene road. A site on a fullerene cage with two or more adjacent pentagons is highly strained and unusually susceptible to attack [3]. So fullerenes satisfying the isolated pentagon rule (IPR) are particularly unreactive towards further addition [22], and thus are the end points on the fullerene road. And indeed, C<sub>60</sub> and C<sub>70</sub> are the first two IPR fullerenes encountered during cage expansion.

Summarizing, the salient features of fullerene synthesis can be understood assuming the coalescence and isomerization of rings into small cages followed by their “fullerene road” inflation into larger fullerenes. While the ring-to-fullerene conversion has been demonstrated, the crucial second step has not been validated experimentally. The pathways for elimination of C<sub>2</sub> from a fullerene have been investigated in theory [23,24]. The incorporation of C<sub>2</sub> in a cage may proceed through similar pathways in reverse. So a carbon dimer may first attach orthogonally to the cage surface (a “stick” intermediate), then rearrange, adding parallel to the surface, to form a “handle,” and eventually dissolve into the wall. If the fullerene road operates, these intermediates may be trapped during cooling by He gas and observed in mobility measurements. However, distinguishing these geometries from normal fullerenes has been beyond the resolving power of previous ion mobility studies [10–13,18–20]. Here we examine the structure of C<sub>n</sub> cations ( $n \sim 40$ –100) employing the new high resolution technique [25].

Ion mobilities were measured using the apparatus described in detail elsewhere [25]. Briefly, the apparatus

consists of a source coupled to a 63 cm long drift tube. Both the source and drift tube are filled with He buffer gas at a pressure of  $\sim 500$  Torr and operated at room temperature. Ions are generated by pulsed 308 nm laser vaporization of a rotating and translating graphite rod or by desorption of a  $C_{60}$  film deposited on a copper substrate. The ions are directed by electric fields to the ion gate and drawn through against a helium counterflow by a voltage gradient. The ions are pulled along the drift tube by a uniform electric field (160 V/cm) and exit through a small aperture at the end. The ions are then mass analyzed by a quadrupole mass spectrometer and detected by an off-axis collision dynode and dual microchannel plates. Drift time distributions are recorded using a multichannel scaler.

Laser desorption of  $C_{60}$  fullerite using a sufficiently high fluence yields a mass distribution of  $C_n^+$  ( $n$  even)

peaking around the integer multiples of  $C_{60}$  mass [26]. We have measured the drift time distributions (DTDs) for clusters with  $n = 54-68$ . Clusters with  $n \leq 60$  exhibit only the usual fullerene peak. For  $n \geq 62$ , multiple features appear at the longer drift time side of the fullerene peak in the DTDs (Fig. 1). The relative intensities of those features decrease with increasing  $n$ . The gap in inverse mobility between the fullerene and the (major) peak with the longest drift time widens rapidly, by about  $100 \text{ V s/m}^2$  per atom, along the progression from  $C_{62}$  to  $C_{68}$ . This rate of increase in the inverse mobility indicates that linear carbon chain(s) are part of the cluster [27]. So we have optimized stick isomers consisting of  $C_{60}$  with chains of various lengths (from two to eight atoms) attached. All calculations were performed using the recently developed self-consistent-charge density-functional

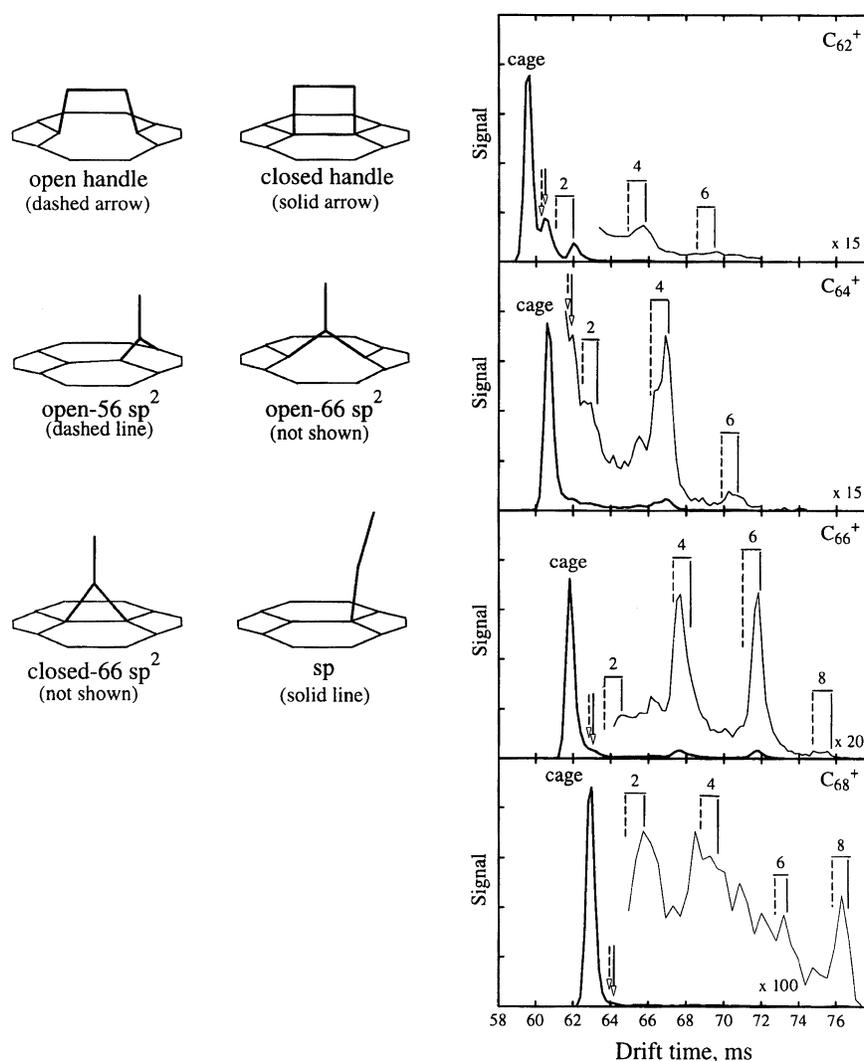


FIG. 1. Drift time distributions measured for  $C_{62}$ ,  $C_{64}$ ,  $C_{66}$ , and  $C_{68}$  cations produced by laser desorption of a  $C_{60}$  film. Drift times calculated for stick and handle geometries are superimposed. Dashed and solid bars are, respectively, for the open-56  $sp^2$  and  $sp$  "sticks"; open- and closed-66  $sp^2$  geometries fall in between. The number of carbons in the chains is given above. Vertical arrows mark handle geometries (on the 66 bond), open (dashed arrow) and closed (solid arrow). Various stick and handle intermediates are pictured on the left.

tight-binding method (DFTB) [28]. For each chain length, we have considered several possibilities for the joint to the fullerene (Fig. 1). A chain may add either to one fullerene atom ( $sp$ ) or across a 56 or 66 bond ( $sp^2$ ) that can remain intact (closed  $sp^2$ ) or break (open  $sp^2$ ) [23,24,27]. DFTB finds the closed-56 adducts to be unstable and convert to open-56 geometries breaking the hinge bond. In the order of increasing energy, other isomers (for either cations or neutrals) are ranked as open-56  $sp^2 < closed-66 sp^2 < open-66 sp^2 < sp$  regardless of stick length. The mobilities for all resulting geometries were evaluated using the trajectory calculations with a realistic cluster-He potential [29]. This potential is constructed from pairwise additive C-He van der Waals interactions plus charge-induced dipole term using the computed partial charges on all cluster atoms [13,29]. This model has been validated for a variety of fullerene-based species [13,27,30,31]. A comparison between the calculated and measured mobilities reveals that the major feature with the longest drift time in the DTDs for all  $C_n^+$  ( $62 \leq n \leq 68$ ) is due to a  $C_{60}-C_{n-60}$  stick isomer (see Fig. 1). For each chain length, drift times computed for possible isomers increase in the following order: open-56  $sp^2 < open-66 sp^2 < closed-66 sp^2 < sp$ . The isomers with  $sp$  attachment agree with the measurements best; however, the accuracy of our mobility calculations and the experimental resolution are not high enough to determine the nature of the chain-to-fullerene joints conclusively. The shapes of some peaks ( $n = 64$ , for example) suggest the possible coexistence of  $sp$  and  $sp^2$  geometries.

All measured DTDs also exhibit minor peaks on either or both sides of those due to  $C_{60}-C_{n-60}$  sticks. The origin of these features becomes obvious if one recalls that the mass envelope around  $C_{60}$  includes smaller and larger fullerenes (such as  $C_{58}$  and  $C_{62}$ ). These can also add chains forming sticks. The mobilities computed for those species fit all the extra peaks except the middle of three major ones for  $C_{62}$ . The DTD for  $C_{62}^+$  is materially different from those for  $n = 64-68$ : There is a major peak between the fullerene and  $C_{n-2}-C-C$  stick. The only reasonable object with a matching calculated mobility is a handle where the  $C-C$  unit is added flat on top of either a 56 or 66 fullerene bond. In DFTB, the product at the 56 site relaxes to the  $sp$  stick. The  $[2 + 2]$  cycloadduct on a 66 bond (Fig. 1) is stable, although it lies about 1 eV above the stick isomers for both neutral and cation. This geometry could be viewed as a cutout from the classic  $[2 + 2]$   $C_{60}$  dimer [32]. The drift time calculated for a similar structure with the hinge bond open (Fig. 1) is very slightly shorter, but so close that this geometry could not be ruled out. In DFTB, it is nearly isoenergetic with the closed-bond handle. We have verified that the peak in question could not be due to any feasible  $C_{62}$  cage, including the low-energy nonfullerene isomers containing heptagons or squares [33]. Small features corresponding to handles also appear for  $n = 64-68$ . An abnormal

abundance of this isomer for  $C_{62}^+$  may be due to the perfect  $C_{60}$  cage being particularly reluctant to incorporate  $C_2$  into the wall, which effectively stabilizes the handle intermediates. Alternatively, it may simply reflect the relative concentrations of reactants: vaporizing  $C_{60}$  makes it much more prominent than other fullerenes produced from it. The sticks and handles reported here are precursors to the  $C_n$  ( $n \geq 122$ ) ball-and-chain dimer and double  $[2 + 2]$   $C_{122}$  cycloadduct ions observed in a hot fullerene plasma [27].

Of course, the starting material in the real synthesis of fullerenes is not  $C_{60}$  but graphite. So we have repeated the measurements using a graphite rod. The mass spectrum for cations shows peaks for all even sizes between about 40 and 100 atoms. The fullerene isomer dominates the DTDs for these clusters. The ring and graphite sheet geometries [10-13,18-20] were not abundant under the conditions employed here. For almost every  $n$  in the  $\sim 50-100$  range, we observed a minor peak (relative abundance of several percent) at a drift time slightly longer than that for the fullerene. Two representative examples are plotted in Fig. 2. For all sizes where a comparison can be made, the mobility of this feature equals that of the  $C_{n-2}-C-C$  stick produced from  $C_{60}$  film. This is illustrated in Fig. 3, where the circles represent species derived from  $C_{60}$  and lines are for those produced from graphite. Most cluster sizes also exhibit trace ( $\sim 1\%$ ) amounts of sticks with four- and six-atom chains, which becomes apparent when an extensive signal averaging is performed. However,

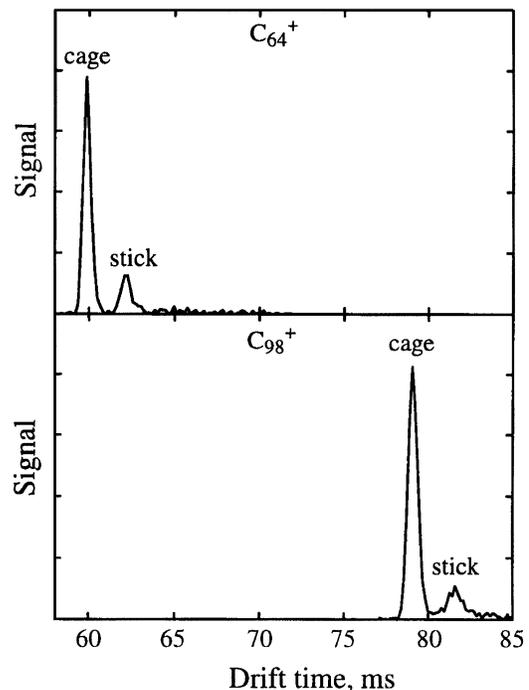


FIG. 2. Portions of the drift time distributions measured for  $C_{64}^+$  and  $C_{98}^+$  generated by laser vaporization of graphite. Scans for other  $C_n^+$  in the  $n \sim 50-100$  range (even  $n$ ) are similar.

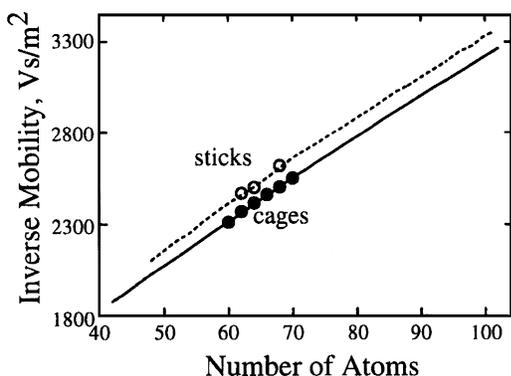


FIG. 3. Mobilities measured for cations produced from graphite (solid line: major peak; dotted line: minor peak) and  $C_{60}$  film (solid and dashed circles for the features assigned, respectively, to  $C_n$  fullerene and  $C_{n-2}$ -C-C sticks).

no handle isomers were found starting from graphite. Starting from graphite, the fullerenes are significantly hotter because of the much higher laser fluence needed for vaporization of graphite as well as the heat released during cage formation, and it could be that the handle intermediates are not trapped. (Calculations [23,24] for  $C_{58}$ -C-C and  $C_{60}$ -C-C indicate that the local minima corresponding to handles are shallower than those for sticks with two-atom chains.) When the sticks are derived from desorption of  $C_{60}$  fullerene, the isomer consisting of a chain attached to  $C_{60}$  normally dominates those involving other cages, while when the sticks are generated by laser vaporization of graphite, the stick with two atoms is by far most prevalent. For example, the  $C_{60}$ -C-C-C-C stick is particularly prominent in the drift time distribution for  $C_{64}^+$  derived from the  $C_{60}$  fullerene, but the dominant stick in DTD for  $C_{64}^+$  produced from graphite is  $C_{62}$ -C-C. These abundances mirror the relative abundances of reactants in the plasma.  $C_{60}$  is dominant when solid  $C_{60}$  is desorbed, but the vaporization of graphite under our conditions produces no "magic" sizes. Peaks due to fullerene +  $C_3$  cations (which might be expected to be abundant) were not observed. It is possible that these are more reactive than the even-numbered stick and handle intermediates and that like some other cationic isomers they do not survive transit through the drift tube.

In conclusion, we have identified new carbon cluster isomers that have mobilities expected for stick and handle geometries. These species are almost certainly intermediates along the "fullerene road." The observation that these intermediates are ubiquitous in a hot carbon plasma is strong support for this mechanism of fullerene growth.

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