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Self-Assembled Novel Materials:
From Transition Metal Clusters to Carbon Nanotubes

by

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ABSTRACT

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By Ting Guo

Novel materials have been self-assembled in the plasma generated by laser vaporization of targets under various conditions. This technique along with the Fourier Transform Ion Cyclotron Resonance (FT-ICR) supersonic cluster beam apparatus and transmission electron microscope (TEM) makes it possible to study both the properties and the growth mechanisms of these new materials. Based on the experimental results and theoretical studies employed the self-consistent (SCF) Hartree-Fock (HF) method and density functional theory (DFT), the growth mechanisms of metallofullerenes referred as extended isolated pentagon rules (EIPR), of single-walled carbon nanotubes denoted as size-limited break-diffusion-formation (SLBDF) mechanism and of multi-walled tubes as lip-lip interaction, have been proposed. The laser-vaporization technique has also been found to be able to produce higher yield and less amorphous carbon covered single-walled nanotubes than does the DC arc discharge.
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I am wholly grateful to Professor Richard E. Smalley, my advisor, for being extremely patient in educating students, including me; passing his gigantic experimental expertise and tremendous knowledge of cluster science to us; and most importantly, bringing a wonderfully creative research environment to young scientists so that they can discover the new territory in chemistry under his guidance.

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PREFACE

Staying in graduate school for five years allows you to share many research projects with fellow students. By the time of graduation, they have helped you write up many of the works that you have done together. As a result, I would like to extend my acknowledgment to Dr. Changming Jin for the pleasant work on the reactivity of transition metal clusters (Cu_n and Au_n with CO and Co with H_2), fullerene derivatives (C_{60}H_n) and the discovery of boron-doped fullerenes on FT-ICR apparatus; to Dr. Yan Chai, Dr. Robert Haufler, Dr. Chang- ming Jin and Dr. Felipe Chibante for the happy collaborations that resulted in the synthesis of La@C_{62}; to Dr. Shigeo Maruyama and Dr. Chuxing Chen for the annealing experiment of transition metal clusters (Ta_{10}, Ta_{12} and Nb_{19}); to Dr. Lihong Wang for the work on FT-ICR; to Dr. Laisheng Wang for the work on Ca@C_{60} and to Dr. Lila Anderson for the study of the property of semiconductor clusters (Ge_n). Their involvement was one of the many critical factors leading to the success of those experiments, which have been elegantly described in their thesis. Therefore, it is possible for me to elaborate the study of the laws that governs the self-assembly of those materials and more that have been synthesized recently in our laboratory.
Chapter 1 Introduction

The interactions, or the chemical bonding, between valence electrons of the elements generally determines the structures that are made of them \([1.1]\). Different structures of the same element, or allotropes, exist due to the intrinsic ability of the element to arrange itself in different manners. Carbon is an excellent example. It can be in the form of graphite, which is the most stable geometry of carbon under normal conditions, diamond, fullerenes or fullerene tubes. You may add amorphous carbon, charcoal, and carbon black into the family. The knob that tunes carbon into one or more of these forms is the environment under which they are synthesized. By adding metals or other elements into the carbon feedstock, it is possible to synthesize a whole new category of carbon based materials, such as metallofullerenes \([1.2]\), doped fullerenes \([1.3]\) and carbon nanotubes \([1.4]\). The outcome depends on the detailed interactions between the added elements and carbon itself. Therefore, for synthesis of new self-assembled materials, the elements themselves and the environment are the only two determining factors. By adjusting these two "knobs" it is possible to dial out any materials that could possibly form.

It should also be emphasized that these arrangement of the elements can only be extended to the limit within which the laws that governs the chemical bonding of elements are followed. In other words, transition states and other
chemically unfavored species will be very hard to assemble by elements themselves. Therefore, studying the laws and the limit to which these laws may apply are crucial to the effective synthesis of self-assembled novel materials.

A direct approach to study these laws is to observe how elements arrange themselves under different, sometimes extreme conditions. Since carbon is the most versatile element in terms of the chemical bonding, it should be very interesting to see how carbon-based materials develop under these conditions. Meanwhile, transition metal elements also demand a close investigation since they are the most important group that could have tremendous applications such as in catalysis [1.5]. Furthermore, the interaction between carbon and transition metal creates many new materials from which our life has been benefited so much [1.6]. Therefore, it is the objective of this research to elucidate the laws that control the chemical bonding of transition metal clusters and mainly, the carbon-based materials.

During the research, many new molecules are discovered and some of them have been isolated [1.7]. Mechanisms that lead to the production of these new materials have been fostered during the study [1.8-1.11]. The experimental results will be presented in Chapter 3 and detailed discussion and proposed models are discussed in Chapter 4 and 5. In the following, a brief account about the cluster science and self-assembly of materials will be given. A rationale of Pentagon Road [1.12] over Fullerene Road [1.13] will be briefly discussed.
1. 1  **Cluster science: past, present and future**

Many metal elements, including Au, Cu, Pb, Sb and Sn, had been recognized and partially isolated in the ancient time as early as 3000 B. C. and their symbols were suggested in as early as tenth century in an old manuscript at St. Mark's, Venice [1.14]. However, the concept of atomic structures was not developed until the end of nineteenth century, and only by then the long history of assuming water, fire, air, earth and ether are the basic elements had finally been put to an end. Since then, the research focus had gone through bulk materials, atomic structures of elements, functional groups and finally, cluster science, registered the progress in both theories and technologies. Recently, nanotechnology is the topic of numerous meetings and conferences and will be the focus in the next ten years or more [1.15].

The original incentive to study the cluster science is to understand the surface phenomena since clusters have very high ratio of surface atoms to internal ones. However, cut a piece of bulk materials does not necessarily give you a piece of material that possesses the properties of the bulk. In fact, the structure of the chipped material could be dramatically different from that of bulk material. The former could experience some basic structure transformation so to satisfy the basic, universal rule of lowering the Gibbs free energy.

A couple of examples are C_{60} [1.16] and Co_{55}, as will be discussed in Chapter 3. They do not posses the structure of the bulk parent materials. The
tendency of minimizing the total energy leads to the novel structures by which these two clusters adopt. In general, transition metal clusters intend to establish a structure with high connectivity, that is, to have maximum number bonds among atoms [1.17], and carbon clusters intend to minimize the number of dangling bonds [1.12].

1.2 Self-assembly of materials

Materials obtained through self-assembly have many advances. One of them is that they can be produced with very high efficiency [1.18]. The competing kinetics of different processes leads to the formation of self-assembled materials, which can be changed by controlling the environment. The forces that invoke the self-assembly range from ionic bond to covalent bond, to hydrogen bond and even to van der Waals force. For the formation of water-nanotubes [1.19], hydrogen bond is crucial. For the self-assembly of DNH deoxyribonucleohelicates, the copper-nucleoside interactions are decisive [1.20]. For the self-assembled apoferritin nanoscale magnet, it is the balance between hydrophilic and hydrophobic forces that makes it happen [1.21]. For the self-assembly of carbon multi-walled nanotubes, the interaction between the adjacent edges of fullerene precursors, as discussed in chapter 5, is critical [1.22]. For the self-assembly of single-walled nanotubes, the interaction between nanometer-sized metal particles and fullerene precursors is crucial [1.23]. For the self-
assembly of transition metal clusters, the interaction between the $d$ band is important [1.24]. Therefore, it is clear that by studying self-assembled materials, we are be able to produce new materials and advance our understanding of chemistry.

As a detailed example, the self-assembly of fullerenes and a rule called IPR will be given in the following.

1.2.1 Self-assembly of fullerenes

The growth mechanisms of fullerenes and metallofullerenes have been pursued ever since the discovery of Buckminsterfullerene in 1985 [1.16]. Many mechanisms have been proposed by different groups based on their observations on fullerene productions by different method [1.25]. Among those proposed mechanisms, Isolated Pentagon Road (IPR) [1.12] has successfully explained that $C_{60}$ can be produced in significant high yield (ca. 30%) from the laser-vaporization fullerene generator in our lab [1.26] (with overall yield as high as 50%). The IPR rule, in which the most energetically favored form of any open graphite sheet is predicted to be the one which (1) is made up solely of pentagons and hexagons; (2) has as many pentagons as possible, while (3) avoiding adjacent pentagons. The chemistry behind these three rules listed above is that the number of dangling bonds should be minimized as a result of lowering the total energy. Therefore, for a highly dispersed carbon vapor in a
fairly high temperature environment, that is, allowing every intermediate state to have enough time to anneal, C\textsubscript{60} is the first fullerene formed, followed by C\textsubscript{70}. The open graphite sheet intermediate states may close before C\textsubscript{60}, but a large energy barrier has to be overcome [1.27]. Another possibility for open sheet to close before size of 60 may be caused by the imperfect annealing due to high carbon density.

It has been suggested [1.16] that laser-vaporization of graphite in high temperature furnace resembles most closely the ideal conditions allowing open carbon networks to anneal into the same curvature as C\textsubscript{60}, the latter is believed to be the energetic most favored geometry for the open carbon sheet with minimal number of dangling bonds. Since 60 is the smallest size of which a carbon network can close without having adjacent pentagons, it possesses both special kinetic stability and thermodynamic stability. As it is stated above, C\textsubscript{60} yield in the laser vaporization apparatus is indeed extremely high. Therefore, IPR is very successful in predicting the special abundance of C\textsubscript{60}.

In addition to C\textsubscript{60}, small fullerenes (<60) have been observed in many experimental conditions [1.28]. One of the growth mechanisms is proposed accordingly as the so-called fullerene road [1.13]. It states that those carbon networks close and form fullerenes at a size as small as 28. Then the C\textsubscript{2} addition prevails. A few molecular dynamics calculations have shown that it is possible for a fullerene to incorporate a C\textsubscript{2} into its cage network [1.29]. An indirect proof of the C\textsubscript{2} addition to fullerenes is the coalescence fullerenes [1.30]. In those
experiments, the product fullerenes have a peak in size distribution at around the mass of their dimers, trimers, etc. However, fullerene road may not be the dominant path for the growth of C_{60} since it had been shown in the earliest experiment that the abundance of C_{60} versus its neighbors could be enhanced 100 times by adjusting the annealing conditions [1.16]. There are a few possibilities: (1) if IPR prevails, the yield of C_{60} is high because it is better annealed and less reactive than other species, closed and open. In the condition, the percentage of small fullerenes is very small since sheets of this range of size stay in the open form. The C_2/C_3 addition mainly occurs to these open sheets, not to small fullerenes, in addition to the fact that small fullerenes should be much less reactive than the open ones. (2) if Fullerene Road dominates, the percentage of small fullerenes as intermediate states should be high at certain stage. Since C_{60} has enough time to anneal into the perfect truncated icosahedral form, and the carbon density in this case is lower than that when the yield of C_{60} is low, the reaction rate between small fullerenes and C_2/C_3 must be smaller, yet the yield of C_{60} is increased, therefore results in a conflicting between the fullerene road and experimental results. This conclusion will be invalid if the overall yield of C_{60} is not increases when annealing condition is achieved since one can argue that the relative enhancement of the yield of C_{60} to other fullerenes is due to the kinetic stability of the well-annealed C_{60}.

Although not been studied, one can easily predict that there is a barrier existing between an annealed open carbon network and the fullerene with the
same number of carbon atoms. The barrier includes rearrangement of the carbon atoms in the open form. The driving force for this rearrangement may come from that fullerenes are more stable than the open networks [1.29], although this statement needs a closer examination. Bower et. al. measured the mobility of carbon clusters and found fullerenes do exist abundantly at the size as small as 32. But the generation of small fullerenes in that experiment is different from that of making 30% of C₆₀ since C₆₀ in their mass spectrum is only slightly higher than its neighbors.

For metallofullerenes, a direct conclusion from the pentagon rule, if the metal atom does not affect the growth mechanism, is that all the endohedral fullerenes should also have maximum abundance at M@C₆₀ and M@C₇₀ in the mass spectrum. Although it is true for most of the cases [1.30], there are some exceptions: U@C₂₆ and M@C₈₂ (M=La, Y, Sc, U, Eu) are either the local or global maximum in the mass spectrum of either directly injected or photo-fragmented metallofullerenes in the FT-ICR laser vaporization experiments [1.31]. Furthermore, not all the metal elements can be attracted into the fullerenes. The self-assembly of these materials is explained by proposing a growth model called extended IPR and will be discussed in Chapter 4.

1.3 Carbon nanotubes
The DC arc discharge of graphite not only has provided the production of macroscopic fullerenes [1.32], it also has given rise to another new form of carbon: multi-walled carbon nanotube [1.33]. These tubes of concentric graphene sheets with different helicity are found in the cathode deposit. It is believed that the extremely high electric field near the cathode sheath and the field emission from these tubes assisted the growth of tubes [1.34]. For some time, it seems that these tubes can not be grown by themselves without the help of high electric field or hydrogen. It turns out now that these tubes can grow when pure graphite is vaporized by a laser light in a high temperature environment. The growth model will be discussed in Chapter 5.

Since the advance of technology is so fast in the last decade, it is possible to assemble a whole new structure through arranging individual atoms [1.35]. It should be pointed out, however, that although this new era of manipulating chemical bonds on the atomic scale is ticking, a solid understanding of how each atom is attached to the operating tool or the building object and how environments affect the bonding is still crucial. In other words, the bonding between elements, whether van der Waals or ionic, is still the key to know and still controls the arrangement of atoms. High efficient synthesis of new materials is definitely favored by a series of stable bonds. Meanwhile, transition states, catalysis, and other processes involved many metastable states in terms of chemical bonding are needed to be investigated in a deeper and higher level. Therefore, although the era of manipulating a single atom is coming, basic
chemistry still applies and the only thing that might be changed is that new laws will be found and replace the old ones.
Chapter 2  Experimental setups

The advance of laser technology benefits many fields [2.1]. Among them, medical surgery, physical chemistry and material science are the biggest beneficiaries. Laser material interactions generate unprecedented playgrounds for studying novel chemical and physical processes, and it has evolved into a powerful, irreplaceable tool in heating, annealing and detecting clusters and other new materials [2.2]. In this work, the laser vaporization technique has been employed to generate carbon plasmas under different circumstances to produce fullerenes, metallofullerenes, metal nanocapsules, multi-walled carbon nanotubes and single-walled carbon nanotubes.

Meanwhile, Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer has been developed into an effectual tool studying stability, structures and reactivity of clusters over the last ten years. The function of FT-ICR ranges from measuring the mass of electrons with eight significant numbers or a giant molecule with mass of more than 1,000,000 amu [2.2], or studying the reactivity of well-annealed clusters [2.3]. The combination of FT-ICR with a laser based cluster beam source gives us an opportunity to study many unprecedented events and materials [2.4].

Other techniques have also been incorporated into the scope of investigating new materials, such as High Performance Liquid Chromatography
(HPLC), X-ray fluorescence spectrometer (XRF), Transmission Electron Microscope (TEM), Scanning Tunneling Microscope (STM), Scanning Electron Microscope (SEM), and more recent Near Field Optical Microscope (NFOM). Among them, TEM is the most effective one in studying the morphology of nano objects produced in this work with an atomic resolution.

In this chapter, important features of supersonic cluster beam source are introduced. The improvements on FT-ICR are then described. The major apparatus that we have been using for producing the materials mentioned above, the furnace based laser vaporization apparatus, is presented in Section 2.2. For the purpose of studying a sublimed film, a sublimator and the process of sublimation are depicted in Section 2.3. General description of XRF is given in Section 2.4. At last, the procedure of preparation of metal-graphite composite rods is described in Section 2.5.

2.1 FT-ICR spectrometer and supersonic cluster beam source.

A general description of this apparatus is shown in Fig. 2.1. It comprises two main compartments: supersonic cluster beam source (SCBS) and FT-ICR mass spectrometer.
2.1.1 Laser vaporization supersonic cluster beam source

It is not surprising that clusters of almost all the elements, especially the refractory ones, can be produced with this technique. During the event, a tightly focused pulsed laser light irradiates the target after the waiting room is filled with inert gases. The atoms or molecules generated by the laser-induced-heat are vaporized into the surrounding inert gas and experience aggregation and condensation to form clusters. When the pressure of the inert gas in the waiting room reaches a critical value [2.5], it undergoes a supersonic expansion.

The Jordan valve generates a 60+/−10 μs burst of gas that goes directly into the waiting room. The throughput of the Jordan valve is in the range of 0.1 to 0.8 Torr•Liter and the peak pressure in the waiting room is about 1-4 atms. The
supersonic beam has the same duration as the inject gas pulse. Cluster size can be controlled by adjusting the delay between the trigger sent to the Jordan valve and that to the Q-switch for laser.

2. 1. 2 Improvements of FT-ICR mass spectrometer

The mechanism of a FT-ICR mass spectrometer has been described in many previous publications from this group [2.6] and by Marshall and Verdun [2.7]. In brief, ions trapped in the ICR cell by the combination of an electrostatic Penning trap along the axial axis and Lorentz force along the radial direction are excited by a radio-frequency electric field applied to a pair of plates called excitation plates, as shown in Fig. 2.1. Since the frequency of cyclotron motion generated by both the RF field across the excitation plates and the uniform magnetic field along the axial direction only depends on the mass to charge ratio of these ions, they are being accelerated constantly by the RF field. When they reach an orbit whose radius is large enough compared to that of the detection plates, it will generate an image current as long as the ions stay in a small packet of diameter much smaller than that of the radius of their cyclotron motion. At this moment, excitation is turned off and the image current is extracted and amplified by an amplifier on the external circuit connected to the detection plates.

Since the resolution of a mass spectrometer is proportional to the time that ions being detected [2.7], lengthening the time that ions spend on the orbits
of their cyclotron motion will increase the mass resolution. To increase the detection time, the number of collisions must be minimized since each collision dephases ions from the original orbit and therefore increases the dimension of the ion packet. Accordingly, the pumping speed, which means a larger bore size or a higher pumping capacity, should be increased; or the excitation time should be shortened so that the total time the clusters spend in the cell can be kept the same while the dephasing effect caused by the collisions during the excitation can be minimized. The new FT-ICR employed both measures, that is, adopting a larger bore size magnet (Φ15 cm) and a higher excitation voltage, to increase the mass resolution.

2.1.2.1 SWIFT amplifier

The new 7 tesla magnet has a bore diameter of 15 cm, which is almost twice as large as the old one. Since the orbital radius of a cyclotron motion is proportion to the excitation amplitude [2.7], the increase of bore size alone demands a larger excitation amplitude, not to mention that less excitation time is preferred. A new SWIFT amplifier that is able to excite 10,000 amu ions into 15 cm orbit within 16 ms to 8 ms is therefore designed and constructed. Fig. 2.2 shows the newly home-designed high voltage SWIFT amplifier. The limiting slew-rate of this circuit is about 400V/μs. It consists of three stages: a x10 wide-
Fig. 2.2 SWIFT amplifier

Fig. 2.3 Excitation waveform generated by SWIFT amplifier
band op-amplifier, followed by a wide-band multiplication stage, and a high voltage amplifier with band-width from 1 kHz to 2 MHz. The new amplifier can supply +/-100 V with band width of 1kHz to 2 MHz. Fig. 2.3 shows the excitation waveform generated by this amplifier.

2. 1. 2. 2 Deceleration pulses and power control

Full automation is the other goal of updating the FT-ICR apparatus. The amplitude of the deceleration pulse and its pulse width are the parameters that are preferred to be adjusted. A simple modification on the SWIFT amplifier shown in Fig. 2.2 leads to a pulse generator that provides a +/-200V DC microsecond pulse for the deceleration tube. The pulse length can be as short as 5 µs and has no up-limit.

The control of later power during the experiment is desired since this was the one of the two parameters, the other one is the decel voltage, that could not be controlled through camac originally. New implementation used an extra trigger from a 3655 module to change the delay between the Q-SW trigger and the fixed time lamp trigger. This implementation has another advantage of keeping the thermal lens effect of the YAG laser constant. Therefore, the laser power can be well controlled through GPIB. Fig. 2.4 shows the measurements of the laser power versus the delay on different runs. As it is shown, the fluctuation
is small at low laser power, which is used to directly desorb out of loosely packed films.

Fig. 2.4 Laser power versus delay between Q-sw and lamp trigger

2.1.2.3 Einsel lens

Since the kinetic energies of heavy ions are so large that their trajectories with moderate divergence angle can be further away from the central axis of the magnetic field before they start the cyclotron motion, by which they are confined into a small radius ion cloud. To correct this problem, an ensel lens is inserted in
the front of the deceleration tube. Through the calculation using Simion [2.8], a pulsed electric field of 10-100 V, 100 µs width is found to be sufficient to resolve this problem.

2.2 Laser vaporization furnace

Studying clusters in vacuum and in the gas phase is fun and full of scientific merits. However, the applications of those clusters demand an isolated form. Therefore, a large quantity of isolated species is highly desired but difficult to achieve. In the lieu of producing such materials, an anaerobic production and processing line is assembled (not self-assembled). Fig. 2.5 shows the furnace based laser vaporization apparatus. It consists of three parts: laser, furnace and collection compartment. The laser is Qustek 581 Q-switched Nd:YAG laser. The plasma is controlled by the following parameters: (1) laser power, (2) beam spot size, (3) furnace temperature, (4) inert gas pressure in the furnace, and (5) gas flow across the target. The gas flow and pressure are controlled by a combination of adjusting a mass flow controller (MKS 1159B) mounted in front of the quartz tube and a needle valve after the quartz tube. The soot is collected by pulling the collector into the collecting chamber while setting the pressure on the inside above the atmosphere and then the soot is swept by the brushes into the
collecting test tube. After enough materials collected, the gate valve is closed and the sample can be transferred anaerobically to the drybox.

![Diagram](image)

**Figure 2.5** Furnace based laser vaporization apparatus

### 2.2.1 Laser generated plasma

The plasma generated by pulsed laser can easily reach 10,000 degree Celsius. All the elements at this temperature are in the gas phase and in the atomic form. Therefore, laser generated plasma is the best source for generating atomic beams. However, the detailed history of the development of laser generated plasma has not been not fully understood. The process can be best
described as a three-step procedure: (1) conversion of energy from light into heat. In this process, laser energy is transferred into the kinetic energies of electrons; (2) collisions between nuclei and electrons result in the heating of nuclei and finally the ejection of the latter. (3) interaction of hot nuclei ( neutrals, positive and negative ions) and cooling gas and condensation of the first. It is the third stage that is not fully understood, and many groups are still working on it [2.9].

The size of the plume that defines the contour of the plasma is observed as a function of the beam size, beam power intensity, pressure of the surrounding gas, and the surrounding temperature. The plume size determines the plasma temperature profile. Assuming the initial temperature is 10,000 K, since the drops of temperature from 10,000 to 3,000 K should not be affected too much by the low temperature surrounding gas, it is concluded that raising the temperature of the furnace dramatically increase the dimension of the region of which plasma temperature is in the range of 1,200 K to 3,000 K. As we will discuss in Chapter 4 and 5, it is this temperature range that affect the growth of fullerenes, metallofullerenes and nanotubes.

2.3 Sublimator and detection routine for sublimed films

One way to extract molecules that have been made in the laser vaporization apparatus but are susceptible to the attacks of oxygen and
moistures is by sublimation in vacuum. Soot contains these molecules can be transferred from the collecting tube into a sublimator in a dry-box. The soot in the sublimator is then sublimes at high temperature. The temperature of the sublimator can be raised to 500 °C to 1000 °C with ramp rate 2 °C per min.

2.3.1 Separation by multiple sublimation

The sublimation of the soot made in LVF produces thin films consisted of a layered structure. This structure stems from the temperature dependence of vapor pressure of different size of fullerenes and metallofullerenes. For example, C_{60} and C_{70} sublime at a take-off temperature of 300-400 °C and C_{64} of 700-800 °C. If the ramp-rate is small enough, the vapor pressure of C_{60} and C_{70} could be greatly reduced when C_{64} starts to sublime at a much higher temperature. Therefore, a layered structure is generated. This layered structure can then be detected and studied by FT-ICR mass spectrometer.

2.3.2 Characterization of sublimed films

The power density of the vaporization laser in FT-ICR spectrometer can be tuned very low so that each laser pulse only desorb a limited number of molecules, or a very thin layer of the film. It is therefore discovered that dimers
and trimers of fullerenes can coalesce in the circumstance [2.10], along with the fact that most of the vaporized as an intact molecule if the laser power density is low enough.

2.4 X-ray fluorescence spectrometer

To quantitatively study metallofullerenes and chartreuse carbon nanotubes of 1000,000 amu, other tools are needed. For the first purpose, an analytical apparatus, X-ray fluorescence spectrometer, of 0.1 μg accuracy is used. Identifying tubes is carried out by TEM.

2.4.1 X-ray fluorescence spectrometer

Since some of the materials are not very soluble in any of the common organic solvent, quantitative measurement can not be obtained by HPLC or FT-ICR. Fortunately, XRF is able to measure metal quantity with accuracy of 0.1 μg for most of metals. Therefore, trace amount of metallofullerenes in the sublimed film can be easily quantitatively determine by XRF. Fig 2.6 gives the schematic description of how an XRF works.
2.5 Preparation of targets

Uniform mixed composite rods are made and used in all the experiments. The metals or metal oxides were mixed with graphite power [Carbone of America] and carbon cement [Dylon] at room temperature. The powder-like paste was then put into a 1/2" diameter mold. The mold was then placed in a hydraulic presser equipped with heating plates [Carvey] and baked at 130 °C for 4-5 hours. The baked rod was then cured at 810 °C for 8 hours in a He gas at 1 atmosphere.
Chapter 3  Experimental results of synthesis via self-assembly and tailoring

The powerful FT-ICR SCB apparatus facilitates the investigation of many kinds of clusters, including transition metals, carbon clusters and its derivatives [3.1]. The ability to simultaneously measure the reactivity and photofragmentation stability of these clusters advances our understanding on their geometric and electronic structures [3.2]. By adopting the laser vaporization technique under different conditions and supplying appropriate starting materials, self-assembled materials are produced in a controllable fashion [3.3].

In the following, two transition metal clusters are studied in Sec. 3.1. The objective is to search the laws that govern the formation of these very complicated clusters. Metal doped endohedral fullerenes are studied in Sec. 3.2 to 3.4. The emphasis is once again on the laws that control the self-assembly of these new materials. In the last section, a new class of materials, carbon nanotubes, is found in the soot produced in furnace based laser vaporization apparatus.

3.1  Transition metal clusters: reactivity and structure

Transition metal clusters (TMC) represent the most attractive research subject in the field of cluster science. The major boost to study TMC stems from
the fabrication of catalysts that have a desired selectivity and activity [3.4]. The parameters that define a transition metal cluster include (1) size or the number of atoms comprises the cluster; (2) the structure; whether it is well annealed or metastable state will dramatically affect the outcome. (3) composition; and (4) ligands. The third one is very important in terms of the selectivity and activity due to the surface segregation of composite clusters [3.5]. The last parameter will not be studied in this work although it is an important issue in many cases.

It is generally considered that geometrical structures affect the chemical reactivity and photo resistivity of these clusters [3.6]. Therefore, results from the study of reactivity and photo stability can be used reversibly to infer the geometrical structures of TMC and so to reveal the self-assembling laws. In the following, each property is used to extract the geometric information.

### 3.1.1 Structure of Nb$_{19}$ and Co$_{55}$

One of the most interesting features is that many isomers can be possessed by a transition metal cluster. This stems from the fact that the cluster under investigation could be in its metastable states rather than the globe minimum. Therefore, different geometric structures may result. In the following Nb$_{19}$ is studied. Fig. 3.1 shows the reactivity pattern of Nb clusters with H$_2$. Clearly the reactivity is very high for these directly injected clusters, whereas only two-thirds of the annealed clusters follows the same pattern. The annealing
was achieved by irradiating the clusters with 50 Hz 150 mj/cm²/pulse XeCl excimer laser for 2-5 seconds followed by thermalizing them with room temperature Ar gas.

Fig. 3.1 The reactivity of Nb₁₉

It is therefore concluded from picture 3.1 that there are at least two isomers existed for Nb₁₉. It also reveals that although transition metal clusters intend to achieve the highest possible connectivity, it is still possible for some of them to stay in metastable states. The bonding behaviors or the valence
electronic structures of these transition metals determine the easiness of reaching the globe minimum.

3.1.2 Fragmentation of transition metal, close shell of 55

The surface energy of small clusters determines the most stable structure since most of the atoms are on the surface [3.7]. For a cluster at size of 13, it is found that it adopts icosahedral shape to minimized its surface energy. The next shell to close is a cubo-octahedron, which needs 55 atoms. To verify the validity

![Co Clusters](image_url)

**Fig. 3.2** Fragmentation of Co clusters
of this idea, photofragmentation experiment is performed on large cobalt clusters. As shown in the upper panel in Fig. 3.2, large Co clusters are injected into the ICR cell. The fragmentation was carried out by irradiation of clusters with 50 Hz XeCl excimer laser at the power density of 200 mJ/pulse/cm² for 3 sec. It is clear that a peak at Co₅₅ is achieved after the fragmentation.

3.2 Minimal endohedral metallofullerenes U@C₂₈

Other examples of self-assembled endohedral metallofullerenes will be presented in the next two subsections. At the presence of alien elements, certain bonding abilities of carbon are enhanced. If the interaction between the alien elements and carbon is strong enough, it can eventually alter the way that they are self-assembled and, instead of favoring the growth of fullerenes, favors the growth of some new species that are otherwise are either kinetically or thermodynamically unfavored. C₂₈ is an example. C₂₈ itself is, at least compared with other large fullerenes, a very reactive fullerene. It behaves as a superatom with a tetravalence with four free electrons localized on the four vertices along the C₃ axis. With the help from other tetravalent elements such as uranium and zirconium, M@C₂₈ becomes a more kinetically and thermodynamically stable molecule. Fig 3.3 shows the mass spectrum obtained in FT-ICR when U/C target is vaporized. As it is shown, U@C₂₈ is the most abundant species in this case. It
is even more abundant than U@C_{60}. The mechanism will be discussed in Section 4.2.2.1.

![Graph of mass vs. m+n](image)

Fig. 3.3 Injection of U@C_n

3.3 Fragmentation of Eu@C_{82}, La@C_{82} and La@C_nB_m (m+n=82)

As it is mentioned in Sec. 3.1, photofragmentation is an effective tool in sensing a particular stable molecule with a special geometry. Because ICR provides a perfect high vacuum environment in which the kinetic stability can be excluded from affecting the outcome of a photofragmentation experiment, the
photo fragmentation stability can then be fully attributed to either special electronic structures or special geometric structures. Fig 3.4 shows the fragmentation results of La@C₈₅B₅₄ (n+m=82). Although La@C₈₅B₅₄ (m+n=82) is the most abundant species in the fragments, it should be pointed out that that peak comprises a series of peaks corresponding to La@C₈₂, La@C₆₉B₅, La@C₆₉B₆ and La@C₇₂B₆. Fig. 3.5 shows the peak at size of 82 in Fig. 3.4 after the isotopical deconvolution. It shows that La@C₈₁B is the most photo stable species. In a similar experiment, Eu@C₈₂ is found to be more stable than its neighbors. On the other hand, La@C₆₂ does not behave very differently from
other metallofullerenes. These results provide an insight about the structures of these metallofullerenes. Since Eu usually stays as +2 oxidation state and B only

![Diagram](image)

Fig. 3.5 Photofragmentation of La@C_{n}B_{m} after deconvolution

has three valence electrons, along with the fact that Eu@C_{82} and La@C_{81}B both possess similar photo stability, it is concluded that these two molecules are isoelectronic, and both are different from that of La@C_{82}. These results seems to be consistent with condensed phase measurement where La in C_{82} is found to donate three electrons to the cage [3.8].
3. 4  **Isolation of M@C_{60}**

The furnace based laser vaporization apparatus and other apparatus allow us to study one of the self-assembled molecules, Y@C_{60} and a not-well-known fullerene C_{74}. Since both of them are not very soluble in any common organic solvents, the study about them has been hindered for some time. In the following, we will provide some overwhelming evidence to show that Y@C_{60} and C_{74} are perfect “health” molecules and it is very possible to isolate them.

3. 4. 1  **Sublimation and characterization of Y@C_{60} and C_{74}**

Since both of them are not very soluble in common organic solvents, the first step of extracting them is sublimation. Soot containing Y@C_{60} or C_{74} made in laser furnace apparatus is sublimed at 1000 °C for 30 min. Fig. 3.6 shows the successive ablations of the film by laser desorption in the FT-ICR apparatus. The top panel in Fig. 3.6 corresponding to the first round of desorption by laser. The second panel corresponds to the second round, followed by the third and the fourth. The average size of clusters in these mass spectra decreases as the desorption deepens. These results reveal the temperature profile of sublimation of different species. As they shown in Fig. 3.6, the sublimation follows that (1)
large fullerenes sublimes at higher temperature and (2) metallofullerenes sublume at higher temperature than empty fullerenes of the same size. Since sublime temperature is a measure of how tight a molecule binds to the bulk, evidently intermolecular forces are in the order of metallofullerenes (n) > fullerenes (n) > fullerenes (n-1)

Fig. 3.6 Laser desorption of the sublimed film of La@Cₙ soot
When soot made from pure carbon is sublimed and then being washed by 50 ml toluene for four times in the air, a surprising result is presented in Fig. 3.7. It is shown that the mass spectrum of positive ions, which is usually a measure of the abundance of neutral species in the sample, contains C\textsubscript{60}, C\textsubscript{70} and C\textsubscript{74}, whereas the negative ion spectrum contains only one peak, C\textsubscript{74}. This indicates that C\textsubscript{74} is a molecule with very electron affinity compared to that of C\textsubscript{60} and C\textsubscript{70}.

Fig. 3.8 Mass spectra of positive and negative ions of the sublimed film of soot made from pure carbon.
When the sublimed film containing Y@C$_{60}$ is washed by 10 ml degassed and dried toluene and 10 ml similarly processed benzonitrile, the residue contains mainly Y@C$_{60}$. The positive ion mass spectrum from FT-ICR is shown in Fig. 3.8. The top panel in Fig. 3.8 shows the composition of the sublimed film before being washed by solvent. The bottom one shows the composition of the residue. It strongly suggests that Y@C$_{60}$ is a perfect molecule that can survive

Fig. 3.8 Mass spectra of the sublimed film (a) and the solvent-washed residue (b)
high temperature sublimation and solvent treatments. If large amount of it can be made, it is possible to prepurify it with this sublimation-wash routine.

3.4.2. Interactions between solvent and Y@C$_{60}$

Table 3.1 lists all the solvents in which the solubility of Y@C$_{60}$ has been measured. Also listed are the dipole moments and dielectric constants of these solvents. It is clear that there is a good correlation between the solubility of Y@C$_{60}$ in these solvents and the corresponding dielectric constants. Based on the simple rule of like dissolves like, it is concluded that Y@C$_{60}$ or its complex within which Y@C$_{60}$ is formed must possess a significant amount dipole moment so that they are more soluble in these solvents of high DC. It should also be pointed out that even the maximum solubility of Y@C$_{60}$, which is achieved in acetonitrile or dimethylformamide, is only 30 µg/ml by XRF measurement [3.9] two order of magnitude smaller than that of C$_{60}$ in toluene [3.10]. Other solvents

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Solubility (C$<em>{60}$ : Y@C$</em>{60}$)</th>
<th>Dipole moment (debye)</th>
<th>Dielectric constant</th>
<th>Solubility (C$_{60}$) (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>&gt; 600 : 1</td>
<td>0.78</td>
<td>2.44</td>
<td>2.8</td>
</tr>
<tr>
<td>carbon disulfide</td>
<td>~ 20 : 1</td>
<td>0.0</td>
<td>2.64</td>
<td>7.9</td>
</tr>
<tr>
<td>α-dichlorobenzene</td>
<td>~ 15 : 1</td>
<td>2.50</td>
<td>9.93</td>
<td>27.0</td>
</tr>
<tr>
<td>pyridine</td>
<td>~ 12 : 1</td>
<td>2.19</td>
<td>12.30</td>
<td>0.89</td>
</tr>
<tr>
<td>benzonitrile</td>
<td>~ 6 : 1</td>
<td>4.17</td>
<td>25.60</td>
<td>0.41</td>
</tr>
<tr>
<td>dimethylformamide</td>
<td>~ 3 : 1</td>
<td>3.82</td>
<td>37.00</td>
<td>?</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>~ 1 : 2</td>
<td>3.80</td>
<td>37.50</td>
<td>0.000</td>
</tr>
</tbody>
</table>
with even higher DC seem to be reactive with either large fullerenes or metallofullerenes and the trend was not followed further down along this line.

3.5 Synthesis of multi-walled carbon nanotubes and single-walled tubes

It is obvious that structures of self-assembled materials depend on the environment. Take carbon with limited number of atoms as an example, the most stable form may not adopt that of bulk. $C_{60}$ is a perfect example. Another one is that microcrystal of diamond is more stable than graphite of the same size [3.11]. Another factor that greatly affect the outcome is the use of catalysts. As it will be shown in sec. 3.5.2 and chapter 5, the presence of catalysts promotes the assembly of otherwise improbable objects made of carbon --- single-walled nano tubes.

3.5.1 Multi-walled tubes

It was believed that electric field or hydrogen has to be around when multi-walled nanotubes are produced [3.12]. As it will be shown below, under adjusted conditions, laser vaporization is also be able to produce multi-walled carbon nanotubes [3.13].
The condition for producing these nanotubes is somewhat different from that for fullerenes. The laser has to be focused more tightly and the flow is at its minimal. The soot collected from the cold collector, from the wall of the quartz tube and the target surface all contains tubes. Fig. 3.9 shows nano objects, long

![Image of carbon tubes made in the laser furnace apparatus](image-url)

**Fig. 3.9** Carbon tubes made in the laser furnace apparatus
and short tubes, collected from the cold collector. The soot was suspended in a methanol solvent and sonicated for 5 min. A small portion of the solution was pipetted onto the lacey carbon TEM copper grid. The image was taken on a JEOL 2010 transmission electron microscope operated at 100 k eV.

As it will be discussed in chapter 5, this discovery forces us to seek new mechanisms, and the idea of lip-lip interaction is so born out.

3.5.2 SWTs

When metal/graphite composite targets are laser vaporized, a new form of carbon is produced. It consists of single-walled carbon nanotubes of about 1 nm in diameter and 10 nm to 5 μm in length. Table 3.2 lists the yields of both fullerenes and single-walled nanotubes as function of metal used and the temperatures.

3.5.1 1200 °C catalytic growth of SWTs from monometal catalysts

Co, Ni, and Pt were used to catalyze the growth of SWTs. Under the condition that maximized the SWTs production (1200 °C, 500 Torr, 50 sccm), Ni was found to be the most effective metal that catalyzes SWTs in the highest yield. Since the yields of SWTs can not be measured with a calibrated method due to the unavailable method that can purify these objects, a relative yield was
given for each catalyst as a comparison to that of Co/Ni, which names as Max based on the TEM images. In this scale, Ni ranked Max/10, Co produced moderate yield of Max/100 and Pt catalyzed very few SWTs (Max/10000), which is shown in Fig. 3.10. Cu alone does not catalyze another tube growth. It is worth noting that single straight SWT can easily be found when the overall yield of SWTs is not high, like that of Pt. When the yield is high, the SWTs intend to tangle with each other and form a highway-like structure, as shown in Fig. 3.11.

Fig. 3.10  A SWT catalyzed by Pt at 1200 °C
3.5.2 Bimetallic catalysts

Different binary systems have also been explored in catalyzing the growth of SWTs. They are Pt/Co, Pt/Ni, Ni/Co, and Cu/Co. The purpose of this part of the research is to try to identify the function of each element in catalyzing the growth of SWTs and how temperature affects the yield of SWTs.

The yield of SWTs catalyzed by these three bimetallic catalysts are in the

Fig. 3.11 SWTs catalyzed by Ni/Co at 1200 °C
decreasing order of Ni/Co>Co/Pt>Ni/Pt>Co/Cu, although the differences among them were small. The TEM image of SWTs catalyzed by Ni/Co is shown in Fig. 3.11.

Among these binary systems, Pt/Co creates the largest increase (100 times) in the yield of SWTs catalyzed by bimetallic catalysts compared to the sum of yields of the corresponding monometal catalysts. As it is shown later, this correlates to not only the magnitudes of decrease in melting temperature of bimetallic alloys but also other special functions possessed by Co/Pt alloy. The yield increases of SWTs form Pt/Ni and Ni/Co are not significantly higher (<10 times) than the sum of Co and Ni or Ni and Pt. Cu did not help at all the increase in the yield if SWTs when it was added into a Co-graphite composite target.

3. 5. 3 Correlation between fullerene yield and that of SWTs

The yields of fullerenes corresponding to above conditions were also measured. The correlation between them and the yields of SWTs are shown in Table 3.2. When the conditions were the same as regular optimized conditions for producing high yield of fullerenes (1200 °C, 500 Torr and 50 sccm), four situations occur: (1) yield of both fullerenes and SWTs were high, as in the Pt/Co case; (2) High yield of fullerenes was obtained and few tubes were found, as in the Pt case; (3) modest yield of fullerenes together with high yield of SWTs
(Co/Ni); and finally (4) modest yield for both fullerenes and SWTs (Ni). On the other hand, when the conditions were varied away from the optimized ones for producing fullerenes, the yield of SWTs could still be high while that of fullerenes drops a little more dramatically, as shown by the experiment on Pt/Co at 1000 °C. Hence the yield of SWTs is less sensitive than that of fullerenes when temperatures were above 900 °C.

3.5.4 Temperature dependence of yield of SWTs and fullerenes

Temperature profile measurements have been performed on two systems: Ni and Pt/Co. Table 1 shows the results of the yields of fullerenes and SWTs at different temperatures. These experiments were conducted to measure the temperature range in which metals catalyze the growth of SWTs. It is shown that catalytic growth of SWTs become sensitive to the temperature when it drops below certain point, e.g., 900 °C. Certain metals are more sensitive than others, e.g., Ni is more sensitive than Pt/Co. Notice also is that the yield of fullerenes in Pt/Co case at 500 °C was enhanced compared to that of pure graphite target. It implies that Pt/Co system might also catalyze the growth of fullerenes at this temperature.

Another new form of carbon is found when Al₄C₃ and graphite composite targets are vaporized in the laser-furnace apparatus. Fig. 3.12 shows the TEM
Table 3.2. The correlation between yields of SWT and fullerenes at different temperatures.

<table>
<thead>
<tr>
<th>Systems</th>
<th>SWT yield</th>
<th>Fullerene Yield</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(C_{60}/C_{70}/C_{76}/C_{84}/Highe)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>None</td>
<td>15%</td>
<td>100 % C</td>
</tr>
<tr>
<td>Co</td>
<td>Max/100</td>
<td>(53/26/12/8) 4.5%</td>
<td>1 at. %</td>
</tr>
<tr>
<td>Co</td>
<td>Max/100</td>
<td>(53/27/12/7) 4.2%</td>
<td>0.6 at. %</td>
</tr>
<tr>
<td>Co/Cu</td>
<td>Max/500</td>
<td>(54/27/11/8) 3.6%</td>
<td>0.6/0.5 at.%</td>
</tr>
<tr>
<td>Co/Ni</td>
<td>Max</td>
<td>(53/24/12/9/2) 8.6%</td>
<td>0.6/0.6 at. %</td>
</tr>
<tr>
<td>Co/Pl</td>
<td>Max</td>
<td>(50/25/12/9/4) 14%</td>
<td>0.6/0.2 at. %</td>
</tr>
<tr>
<td>Co/Pl</td>
<td>Max/(2-5)</td>
<td>(54/29/7/5) 2%</td>
<td>0.6/0.1 at. %</td>
</tr>
<tr>
<td>Co/Pl</td>
<td>Max/50</td>
<td>(52/48) 0.043%</td>
<td>0.6/0.2 at. %</td>
</tr>
<tr>
<td>Co/Pl</td>
<td>Max/2500</td>
<td>&lt;10°</td>
<td>0.6/0.2 at. %</td>
</tr>
<tr>
<td>Nb</td>
<td>None</td>
<td>(48/25/13/12/2) 5.8%</td>
<td>0.6 at. %</td>
</tr>
<tr>
<td>Ni</td>
<td>Max/10</td>
<td>(58/26/10/6) 4.7%</td>
<td>0.6 at. %</td>
</tr>
<tr>
<td>Ni</td>
<td>Max/50</td>
<td>(63/29/4/4) 2.7%</td>
<td>0.6 at. %</td>
</tr>
<tr>
<td>Ni</td>
<td>None</td>
<td>(50/50) 0.006 %</td>
<td>0.6 at. %</td>
</tr>
<tr>
<td>Ni/Pl</td>
<td>Max/(2-5)</td>
<td>(58/26/10/6) 6.6%</td>
<td>0.6/0.2 %</td>
</tr>
<tr>
<td>Pt</td>
<td>&lt;Max/10000</td>
<td>(46/25/13/11/5) 11.3%</td>
<td>0.2 at. %</td>
</tr>
</tbody>
</table>

Images of these objects. It comprises carbon nanotubes of 6-8 nm in diameter with possibly Al_{4}C_{3} on the inside. The number of carbon layers is in the range of 2 to 10. It is somewhat surprising that such carbide “sticks” can form with uniform
Fig. 3.12 TEM image of aluminum carbide nano sticks covered with nanotubes
diameters. Further experiments should be done to see if the shape can be
optimized.
Chapter 4 Growth model for self-assembled doped and metallofullerenes

The self-assembled fullerenes [4.1], endohedral metallofullerenes [4.2], doped fullerenes [4.3] and endohedral doped metallofullerenes [4.4] furnish a series of examples of how atoms are bonded to each other according to their intrinsic bonding abilities or valence structures. Those are different from shooting high speed He atoms at buckyballs to form endohedral fullerenes [4.5]. The latter is not a product due to self-assembling. IPR [4.6] reveals a very important feature for the understanding of the self-assembly ability possessed by carbon. However, the journey of discovering the laws that govern the self-assembly of carbon have not been completed yet. More direct experimental evidence and higher level of theoretical studies are needed to thoroughly resolve the growth of many forms of carbon including the laws that govern the self-assembly of metallofullerenes and doped fullerenes. The objectives of this chapter are to study theoretically and experimentally (1) the causes for the growth of metallofullerenes and doped fullerenes and (2) how alien atoms affect the carbon cage. The second issue is critical to the understanding of the products of self-assembly. Other example about self-assembled transition metal clusters includes Nb$_{19}$, Co$_{55}$ and metal-car Sc$_8$B$_{12}$.

In the section 4.1, the structures of transition metal clusters are proposed to account for the difference in reactivity between the isomers and the special
photo fragmentation stability. SCF-HF method is then employed predicting and elucidating results of calculation on doped fullerenes and endohedral metallofullerenes, especially the size and structural effects of metal elements on the formation of endohedral metallofullerenes and the endohedral metallofullerene bonding structures. In Sec. 4.3 a new model involving the concept of electronegativity is proposed to explain the growth of metallofullerenes.

4.1 Structures of transition metal clusters

Although many ligand-transition metal complexes can be synthesized in solution [4.7], the laws that govern the self-assembly of TMC have mostly been learned in the gas phase [4.8]. Since chemisorption of reactants on transition metal clusters depends on parameters such as the flatness of surfaces [4.9], entrance barriers of the reaction channel [4.10] and the available coordination of the surface atoms [4.11], and all these depend on the structures of clusters, it has become an important method to study the structures of TMC in the gas phase. For Nb$_{19}$, the chemisorption experiment of H$_2$ on it reveals that there are two isomers [4.12], as shown in Fig. 4.1. One of them has a more flatter surface than the other, hence less reactive toward H$_2$; although the second possesses a higher connectivity, hence a more stable form. Since the "annealing" only transforms one-third of the reactive isomer into the unreactive one, it is
conceivable that the reactive structure is only a local minimum on the potential surface. This reveals another feature concerning the self-assembled TMC: it may have many isomers that have similar stability though different chemical and physical properties. If we can control the environment so to control the instantaneous structures of TMC, we may have a whole new class of nanoscale materials whose properties can be controlled.

![Fig. 4.1 Structures of reactive (a) and unreactive (b) Nb$_{19}$.](image)

The explanation for the special photo-stability of Co$_{55}$ could be simply due to its geometric shell closing. It has been found earlier that small metal clusters adopted an even more dense closed packing than that of FCC [4.13]. The clusters will pack in such a way that a shell of twelve atoms surrounds the core atom to form icosahedral $M_{13}$, in the next shell, forty-two atoms will pack around it to form cubo-octahedral $M_{55}$. The fourth shell contains 92 atoms. Since the shell close at 55, each atom on the surface, including the one on the edges, has
9 neighbors. When the size is not equal to 55, there are certain atoms that have less than 9 neighbors, therefore with less binding energy. It should be pointed out, however, that the path leading to the structure of 55 on the potential surface could be different from metal to metal. Fe_{55}, for example, does not possess a clear peak at peak 55 as C_{55} in the photofragmentation experiment under similar conditions [4.14]. Since the forces that control the structures are due to the interactions between the valence electrons, it is possible that Fe clusters have different paths when they are fragmented down to small ones since it has one less valence electron than that of Co. The detailed calculations on the surface energy of these clusters of different structures may explain the experimental results.

4.2 SCF-HF ab initio predictions

The calculations of applying TURBOMOLE to fullerene problems were traced back to 1990 when J. Cioslowski et. al. [4.15] and G. E. Scuseria [4.16] used it for the first time to study fullerenes and metallofullerenes. It has been proved in the last five years that this package is capable of predicting and explaining many molecules, including endohedral metallofullerenes and doped fullerenes, and processes involved carbon base materials [4.17]. Total energies, ionization potentials (IP), HOMO-LUMP gaps, and Mulliken population analysis based on this method have been predicted for the above species with adequate
accuracy. The extension of TURBOMOLE by applying density functional
theory allows us to estimate the binding energies more accurately since the
correlation energy is considered [4.18].

The theoretical study of these molecules is significant because many
insightful explanations can only be obtained through these precise calculations
for such large molecules. The results we have obtained by employing SCF-HF
method in studying metallofullerenes and doped fullerenes will be presented in
the following sections. The emphasis will be on the formation mechanisms of
these molecules.

4. 2. 1 Computational details

The results presented in following were obtained employing the direct
SCF-HF method [4.19] as implemented in the TURBOMOLE package [4.20].
Equilibrium geometry was calculated employing analytical gradient techniques.
The basis set used for carbon was a double-zeta contraction of van Duijneveldt
primitive set (7s3p/4s2p) [4.21]. Similar basis sets of double zeta quality were
used for Mg (10s6p/6s2p), Al, Si, and S (11s7p/6s4p) while (14s9p5d/8s5p3d)
from Wachters for Sc and Ti, (14s11p2d/7s5p2d) for Ge, and (16s13p7d) and
(17s11p8d) for Sn and Zr [4.22] are used for the calculations on M@C_{28}. In the
study of Ca@C_{n}, a (12s6p/8s4p) contraction [4.23] basis set was used for Ca.
Additional valence 4p function [4.24] was tested and the effect of these functions
was found to be very small. The bonding structure of Sc@C$_{60}$ was studied with extended Wachters (14s9p5d/10s8p4d) for scandium, in which two $p$ and one $d$ function are added to the original Wachters (14s9p5d/8s5p3d) [4.25]. To calculate the total energy of Sc@C$_{60}$ with Sc at different positions on the inside of C$_{60}$, the geometry is optimized for each fixed Sc position on the $C_5$ symmetry axis. For the work on boron doped endohedral fullerenes, the double zeta basis sets with default contractions were used for boron (8s4p/4s2p), sodium (10s6p/6s2p), and calcium (12s6p/8s4p) [4.26]. At last, the basis sets of Sc and Ti are (14s9p5d/8s5p3d) from Wachters [4.22] when Sc$_{6}$B$_{12}$ was calculated.

To obtain more accurate binding energies, higher level of theory, the density functional theory, also known as Becke-Lee-yang-Parr (BLYP) model, that includes the electron correlation effects was employed [4.18]. BLYP method has been employed to perform single energy point calculations by using the optimized geometry from SCF-HF method.

All calculations were performed on a HP-950 workstation at Rice University.

4.2.2 Size effect of metal elements on the formation of M@C$_n$

The interaction between metal atoms and fullerenes or fullerene precursors are very important in order to understand the formation of endohedral metallofullerenes. The approach used here is to study (1) the metals that
can be trapped inside the smallest fullerene C_{28}, as discussed in Section 4.2.2.1; (2) the smallest size of fullerene that can trap certain metal on the inside if it is not C_{28}, which is studied in Section 4.2.2.2; and (3) results of typical bonding structures of metallofullerenes M@C_{60} and of doped fullerenes to understand the interaction between the valence electrons of metal and carbon atoms are presented in Section 4.2.3.

4.2.2.1 M@C_{28}

Although the first experimental evidence of metallofullerenes was found right after the discovery of C_{60} [4.27], it was not until 1988 that unambiguous results of endohedral structure were obtained by studying these metallofullerenes in FT-ICR cluster apparatus [4.28]. In that experiment, M@C_{60} was selected and irradiated with strong excimer laser light. It is found that the fragmentation products consisted of M@C_{n} (n=60, 58, 56...m_{S}). The smallest size of fullerene that can wrap an element on its inside depends on the element M. For example, m_{S}=44 for Ca@C_{n}, and m_{S}=36 for La@C_{n} [4.29]. Recent experiments showed that m_{S}=28 for U@C_{n} [4.30] and Sc@C_{n}, and m_{S}=30 for Y@C_{n} [4.31], as presented in chapter 3. Under similar conditions, the smallest empty fullerene was found to be C_{32}.

These experimental results indicate that metal elements are indeed able to alter the way that carbon is assembled. They also provide information about
the mechanisms of the formation of fullerenes and metallofullerenes. In the following, the binding energies of M@C\textsubscript{28} will be calculated. It is amazing that an excellent agreement has been found between the predicted binding energies of M@C\textsubscript{28} and the experimental results.

Figure 4.1 shows the optimized geometric structure of C\textsubscript{28} and/or M@C\textsubscript{28} at T\textsubscript{d} symmetry. The indices on the picture indicate the symmetrically independent atoms.

![Structure of C\textsubscript{28}/M@C\textsubscript{28}](image)

The electronic ground states of the molecules are shown in Table 4.1. The T\textsubscript{d} symmetry was applied to C\textsubscript{28} and C\textsubscript{28}H\textsubscript{4}, C\textsubscript{28}F\textsubscript{4} and all the M@C\textsubscript{28}. The ground state of C\textsubscript{28} has a high spin open-shell electronic structure, which have one electron on a\textsuperscript{1} and three other electrons on f\textsuperscript{2} orbital. The total energy of the ground state is far below the next closed-shell state. These four electrons correspond to four dangling bonds located at four vertices on four C\textsubscript{3} axes in T\textsubscript{d}. 
symmetry of $C_{2v}$. This is corroborated by the Mulliken population analysis, which shows that these four electrons are mainly contributed from the carbon atoms at the four vertices on $C_3$ axis of $C_{2v}$. The ground state of $C_{2v}$ is not subjected to

Table 4.1 Theoretical predictions for $C_{2v}$ and derivatives at DZ/SCF-HF level of theory in $T_d$ symmetry$^a$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Energy</th>
<th>HOMO</th>
<th>LUMO</th>
<th>IP(eV)</th>
<th>$\Delta$(HOMO-LUMO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{2v}$ ($A_2$)</td>
<td>-1058.30220</td>
<td>-0.320(t_2)</td>
<td>+0.055(e)</td>
<td>8.7</td>
<td>0.182</td>
</tr>
<tr>
<td>$C_{2v}$H_4 ($A_1$)</td>
<td>-1060.85293</td>
<td>-0.295(t_1)</td>
<td>+0.038(t_2)</td>
<td>8.0</td>
<td>0.167</td>
</tr>
<tr>
<td>AlC$_{2v}$ ($A_1$)</td>
<td>-1300.00552</td>
<td>-0.300(t_2)</td>
<td>-0.007(a_1)</td>
<td>8.2</td>
<td>0.167</td>
</tr>
<tr>
<td>SiC$_{2v}$ ($T_1$)</td>
<td>-1346.84109</td>
<td>-0.278(a_1)</td>
<td>+0.019(e)</td>
<td>7.6</td>
<td>0.167</td>
</tr>
<tr>
<td>GeC$_{2v}$ ($B_2$)</td>
<td>-3133.20987</td>
<td>-0.298(t_2)</td>
<td>+0.019(a_1)</td>
<td>8.0</td>
<td>0.170</td>
</tr>
<tr>
<td>SnC$_{2v}$ ($A_1$)</td>
<td>-7077.15155</td>
<td>-0.324(t_2)</td>
<td>-0.077(t_1)</td>
<td>8.8</td>
<td>0.247</td>
</tr>
<tr>
<td>MgC$_{2v}$ ($T_1$)</td>
<td>-1257.73862</td>
<td>-0.290(a_1)</td>
<td>+0.015(e)</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>CaC$_{2v}$ ($T_1$)</td>
<td>-1734.62352</td>
<td>-0.293(a_1)</td>
<td>+0.077(e)</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>ScC$_{2v}$ ($B_1$)</td>
<td>-1445.09180</td>
<td>-0.103(t_2)</td>
<td>+0.015(e)</td>
<td>8.1</td>
<td>0.118</td>
</tr>
<tr>
<td>TiC$_{2v}$ ($A_1$)</td>
<td>-1818.05189</td>
<td>-0.305(t_2)</td>
<td>+0.007(e)</td>
<td>8.3</td>
<td>0.300</td>
</tr>
<tr>
<td>ZrC$_{2v}$ ($A_1$)</td>
<td>-1906.57900</td>
<td>-0.320(a_1)</td>
<td>-0.020(t_2)</td>
<td>8.7</td>
<td>0.300</td>
</tr>
<tr>
<td>ZrC$_{2v}$ ($A_1$)</td>
<td>-4597.32717</td>
<td>-0.315(a_1)</td>
<td>+0.002(e)</td>
<td>8.6</td>
<td>0.317</td>
</tr>
</tbody>
</table>

$^a$ All energies in Hartrees except IP in eV.

Jahn-Teller distortion. On the other hand, it should be noted that MgC$_{2v}$, CaC$_{2v}$, and SiC$_{2v}$ all have open-shell electronic ground states that are subjected to the Jahn-Teller distortion. Therefore, a lower symmetry has to be adopted for these molecules.

Table 4.2 presents the total energies of these molecules at their optimized geometries in $C_{2v}$ symmetry. It should be pointed out that the energy lowering in
$C_{2v}$ symmetry compared to that in $T_d$ for those molecules having electronic ground states that are not subjected to Jahn-Teller distortion are due to the symmetry breaking [4.32]. Ti@C$_{28}$ is an example. However, since C$_{28}$ at the same geometry obtained from $T_d$ symmetry possesses the same total energy

Table 4.2 Theoretical predictions for C$_{28}$ and derivatives at DZ/SCF-HF level of theory in $C_{2v}$ symmetry$^a$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Energy (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>IP (eV)</th>
<th>$\Delta E$ (eV) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{28}$ ($^6A_2$)</td>
<td>-1058.30670</td>
<td>-0.262(t2)</td>
<td>-0.080(a1)</td>
<td>7.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Al@C$_{28}$ ($^2A_1$)</td>
<td>-1300.02110</td>
<td>-0.302(t2)</td>
<td>-0.004(a1)</td>
<td>8.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Si@C$_{28}$ ($^2A_1$)</td>
<td>-1346.87915</td>
<td>-0.296(t2)</td>
<td>+0.000(a1)</td>
<td>8.1</td>
<td>1.0</td>
</tr>
<tr>
<td>Sn@C$_{28}$ ($^2A_1$)</td>
<td>-7077.15155</td>
<td>-0.324(t2)</td>
<td>-0.077(t1)</td>
<td>8.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Mg@C$_{28}$ ($^4B_2$)</td>
<td>-1257.81049</td>
<td>-0.301(a1)</td>
<td>+0.017(e)</td>
<td>7.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Ca@C$_{28}$ ($^4A_2$)</td>
<td>-1734.63660</td>
<td>-0.296(a1)</td>
<td>+0.000(e)</td>
<td>8.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Sc@C$_{28}$ ($^2A_1$)</td>
<td>-1818.06723</td>
<td>-0.308(a1)</td>
<td>+0.002(t2)</td>
<td>8.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Ti@C$_{28}$ ($^1A_1$)</td>
<td>-1906.64494</td>
<td>-0.313(a1)</td>
<td>-0.000(t2)</td>
<td>8.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Zr@C$_{28}$ ($^1A_1$)</td>
<td>-4597.32717</td>
<td>-0.315(a1)</td>
<td>+0.002(e)</td>
<td>8.6</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^a$ All energies in Hartrees except IP in eV.

$^b$ Energy lowering due to symmetry relaxation from $T_d$ to $C_{2v}$.

As that in $C_{2v}$ symmetry, symmetry breaking does not happen to C$_{28}$. Further calculations included electron correlation effect indicate that C$_{28}$ is indeed in $T_d$ as the ground state symmetry. For other molecules except Sn@C$_{28}$ and Zr@C$_{28}$, it seems $C_{2v}$ is the symmetry of their electronic ground states even though the ground states predicted in $T_d$ symmetry are not subjected to the Jahn-Teller distortion.
The predicted binding energies for these molecules employed the density functional theory extended from SCF-HF are presented in Table 4.3. It is clearly that a good correlation exists between experimental results and theoretical predictions. The Mulliken population analysis shows the net charge on Zr is only +0.3, indicating a significant amount of covalent bond between it and the frontier orbital of C_{28} cage.

Table 4.3 Calculated thermodynamic stability of M@C_{28}.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Symmetry</th>
<th>Electronic states</th>
<th>De-E(C_{28})</th>
<th>Forms Endo at C_{28}</th>
<th>Ionic radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{28}H_{4}^{+}</td>
<td>T_{d}</td>
<td>^{1}A_{1}</td>
<td>-8.0</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Al@C_{28}</td>
<td>C_{2v}</td>
<td>^{1}A_{1}</td>
<td>3.7</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Si@C_{28}</td>
<td>C_{2v}</td>
<td>^{1}A_{1}</td>
<td>7.8</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Ge@C_{28}</td>
<td>C_{2v}</td>
<td>^{1}B_{2}</td>
<td>6.3</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Sn@C_{28}</td>
<td>T_{d}</td>
<td>^{1}A_{1}</td>
<td>8.0</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Mg@C_{28}</td>
<td>C_{2v}</td>
<td>^{1}B_{2}</td>
<td>1.6</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Ca@C_{28}</td>
<td>C_{2v}</td>
<td>^{1}A_{2}</td>
<td>4.5</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>S@C_{28}</td>
<td>C_{2v}</td>
<td>^{3}B_{1}</td>
<td>15.2</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Sc@C_{28}</td>
<td>C_{2v}</td>
<td>^{1}A_{1}</td>
<td>-1.5</td>
<td>Yes</td>
<td>0.89 (+3)</td>
</tr>
<tr>
<td>Ti@C_{28}</td>
<td>C_{2v}</td>
<td>^{1}A_{2}</td>
<td>0.8</td>
<td>Very small</td>
<td>0.68 (+4)</td>
</tr>
<tr>
<td>Zr@C_{28}</td>
<td>T_{d}</td>
<td>^{1}A_{1}</td>
<td>-2.8</td>
<td>Yes</td>
<td>0.86 (+4)</td>
</tr>
</tbody>
</table>

Considering that SCF-HF always underestimates the stabilizing energy, it is obvious that Zr@C_{28} and Sc@C_{28} should be observed experimentally, which turns out to be true. Fig. 4.3 shows the ICR mass spectrum when ZrO_{2}/graphite pressed disk is vaporized. It shows that Zr@C_{28} is the smallest metallofullerenes. It should note that all the testing experiment has been performed in similar conditions. If an element has once been found to be able to make endohedral
metallofullerenes, the variation of conditions will not affect that result; if it cannot make into endohedral fullerenes in a specific condition, it is almost impossible to make it happen by changing the experimental conditions. Therefore, it is the intrinsic properties and "mutual agreement" between carbon and the other metal elements that determines whether an element can be trapped on the inside of a fullerene.

Fig. 4.3 FT-ICR mass spectrum of Zr endohedral fullerenes
4.2.2.2 The role of endohedral atom in the formation of Ca@Cₙ

In this section, calcium endohedral metallofullerenes are studied in order to illustrate the correlation between the binding energies and the relative abundance of metallofullerenes [4.33]. As we know from the last section that Ca does not form Ca@C₂₈ complex. Will it form any endohedral metallofullerenes? What could be the possible switch for the formation of endohedral fullerenes? Based on the calculations shown below and the results from the last section, an extended pentagon road rule (EIPR) is proposed so that it can give correct predictions about what happens if metal elements are presented with the carbon atoms.

The predicted ground states, symmetries, total energies of calcium endohedral fullerenes, the energies of the corresponding empty fullerenes, the energies of HOMO-LUMO, and the binding energies at SCF-HF level of theory are presented in Table 4.4. The symmetries of metallofullerenes are kept the

Table 4.4. SCF predictions of binding energies of Ca@Cₙ (n=28, 36, 40, 42, 44, 50, 60)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Symmetry</th>
<th>E(Ca@Cₙ)</th>
<th>E(Cₙ)</th>
<th>HOMO-LUMO</th>
<th>Binding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca@C₂₈ (S'A₂)</td>
<td>C₂ᵥ</td>
<td>-1734.63660</td>
<td>-1058.30674</td>
<td>-0.3300/0.000</td>
<td>-4.5</td>
</tr>
<tr>
<td>Ca@C₃₆ (1A₁)</td>
<td>D₂⁾d</td>
<td>-2037.41372</td>
<td>-1360.92820</td>
<td>-0.247/-0.079</td>
<td>-0.3</td>
</tr>
<tr>
<td>Ca@C₴₀ (1B₂)</td>
<td>D₂</td>
<td>-2188.81683</td>
<td>-1512.29640</td>
<td>-0.238/-0.058</td>
<td>+0.6</td>
</tr>
<tr>
<td>Ca@C₴₂ (1A₁)</td>
<td>D₃</td>
<td>-2264.48140</td>
<td>-1587.96148</td>
<td>-0.237/-0.068</td>
<td>+0.7</td>
</tr>
<tr>
<td>Ca@C₴₄ (1A)</td>
<td>D₂</td>
<td>-2340.18528</td>
<td>-1663.63775</td>
<td>-0.245/-0.067</td>
<td>+1.4</td>
</tr>
<tr>
<td>Ca@C₵₀ (1A₁)</td>
<td>C₅ᵥ</td>
<td>-2567.23905</td>
<td>-1890.67917</td>
<td>-0.243/-0.051</td>
<td>+1.7</td>
</tr>
<tr>
<td>Ca@C₶₀ (S'A₂)</td>
<td>C₅ᵥ</td>
<td>-2945.59326</td>
<td>-2269.14567</td>
<td>-0.187/-0.040</td>
<td>-1.3</td>
</tr>
</tbody>
</table>
* Open-shell electronic state.

same as their corresponding empty ones [4.34]. Even though the symmetries of the medium size metallofullerenes, Ca@C_{36} to Ca@C_{44}, prevent Ca from moving away from the center, no substantial amount of energies is expected to gain by lowering the symmetry since Ca is too large for these sizes. The results of Ca@C_{50} support this assumption. In that case, Ca is allowed to move along the \( C_{5v} \) axis and the predicted Ca site is only 0.0005 Å away from the center. In addition, Ca@C_{44} in \( C_2 \) and \( C_1 \) symmetries are also examined, and the results are exactly the same as that in \( D_2 \) symmetry.

Almost all the electronic ground states predicted for the calcium metallofullerenes studied has a closed-shell ground state, except Ca@C_{28} and Ca@C_{60}. The HOMO-LUMO gaps are in the range of 4.57 to 5.22 eV, which are less than that of empty fullerenes (in the range of 7-8 eV at SCF-HF level of theory). It indicates that these species are more reactive than empty fullerenes and probably more readily be oxidized than reduced. This later property is tested by the reaction of trimethylamine (TMA), which has a lone pair of electrons. It is found that C_{60} is more reactive toward TMA than do the Ca@C_{60}, as shown in Fig. 4.3. Other properties can be tested when the isolated Ca@C_{60} is available.

The binding energy of calcium metallofullerenes is defined as the difference between the total energy of a metallofullerene and the sum of energies of calcium atom and the corresponding empty fullerenes. As shown in
Table 4.4, the binding energy starts to become positive at the size of $\text{Ca@C}_{40}$. Double its value at $\text{Ca@C}_{44}$, and reach the maximum at $\text{Ca@C}_{50}$. The binding energy turns out to be negative for $\text{Ca@C}_{60}$ with current basis set. Therefore, the calcium on the inside of $\text{C}_{60}$ actually destabilizes the whole molecule a little bit. On the other hand, calcium can stabilize, to different extents, the metallofullerene products of $\text{Ca@C}_{42}$, $\text{Ca@C}_{44}$, and $\text{Ca@C}_{50}$.

![Graph showing mass spectra](image)

Fig. 4.4 Reaction of TMA with $\text{C}_{60}$ and $\text{Ca@C}_{60}$
Similar results were shown in Table 4.5, in which the BLYP DFT binding energies were calculated using the SCF-HF optimized geometries. The DFT method is more accurate in predicting the binding energy since correlation energy is considered. As it shown in Table 4.5, the general trends are exactly the same as predicted by SCF-HF.

The above results seem to be a little surprising since Ca@C\textsubscript{60} is still the primitive product. However, an excellent correlation has been found between the magnitude of binding energy and the enhancement of the relative abundance of metallofullerenes. The relative abundance of Ca@C\textsubscript{2n} and C\textsubscript{2n} generated in the FT-ICR supersonic beam cluster apparatus is shown in Fig. 4.5. The dotted line (circle, solid) represents the contour of mass spectrum of empty fullerenes, and the solid line (triangle, solid) represents the contour of mass spectrum of calcium endohedral fullerenes. The third solid line (box, solid) represents the ratio of the signal intensities of Ca@C\textsubscript{2n} to the corresponding C\textsubscript{2n}. It is obvious that there is a good correlation between these ratios and the magnitude of the binding.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>E(Ca@C\textsubscript{n})</th>
<th>E(C\textsubscript{n})</th>
<th>Binding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca@C\textsubscript{28}</td>
<td>-1741.93646</td>
<td>-1064.66812</td>
<td>-1.1</td>
</tr>
<tr>
<td>Ca@C\textsubscript{36}</td>
<td>-2046.47883</td>
<td>-1369.16150</td>
<td>0.3</td>
</tr>
<tr>
<td>Ca@C\textsubscript{40}</td>
<td>-2198.75287</td>
<td>-1521.39560</td>
<td>1.3</td>
</tr>
<tr>
<td>Ca@C\textsubscript{42}</td>
<td>-2274.87821</td>
<td>-1597.51103</td>
<td>1.6</td>
</tr>
<tr>
<td>Ca@C\textsubscript{44}</td>
<td>-2351.03127</td>
<td>-1673.63393</td>
<td>2.4</td>
</tr>
<tr>
<td>Ca@C\textsubscript{50}</td>
<td>-2579.40118</td>
<td>-1902.01541</td>
<td>2.1</td>
</tr>
<tr>
<td>Ca@C\textsubscript{60}</td>
<td>-2959.98329</td>
<td>-2282.68197</td>
<td>-0.2</td>
</tr>
</tbody>
</table>
energies. This good correlation is best indicated by the big increase at Ca@C_{44}, maximum at Ca@C_{50}, and a big decrease from Ca@C_{50} to Ca@C_{60}.

Therefore, the binding energies studied in this work serve a signed offset to the enhancement of relative abundance of metallofullerenes to their empty fullerene counterparts. If the offset is large enough it can affect the way the metallofullerenes are produced.

![Graph showing abundance and relative enhancement of metallofullerenes versus cluster size](image)

Fig. 4.5 Ca@C_n versus C_n

Since IPR is based upon the assumption that the most energetic stable form of an open sheet at size smaller than 60 is in the same curvature as that of
C\textsubscript{60}, it is conceivable that this form could be changed when metal atoms are around. Results shown above support this idea. Therefore, open sheets with size smaller than 60 could be closed much more easily when certain types of metals are around. We will elucidate in Section 4.3 about what property of metals is crucial in order for them to be trapped on the inside of fullerenes. Consequently, isolated pentagon rules have to be revised to incorporate the interaction between the metal elements and the surrounding carbon networks. In these cases, extended pentagon rules are applied, which state that metal atoms can either lower the closing barriers or make the closing process to be energetically favored.

Ca@C\textsubscript{17} may not be the best system to illustrate the possibility of charting the pentagon road since the interaction between Ca and carbon cages is mainly ionic and the energy gained by inserting the Ca is not large enough to change the abundance of the primitive species such as that of Ca@C\textsubscript{60} and Ca@C\textsubscript{70}. On the other hand, the advantage is its simplicity so that the calculations are still affordable and instructive.

We have to emphasize that the absolute value of binding energies may vary if the quality of the basis set changed. For Example, the binding energy for Ca@C\textsubscript{60} may become a little bit positive if more p and d functions were added to the Ca basis set. But we do not expect any dramatic change in the trend of the binding energies.
4. 2. 3  

**Cage distortion in doped and metallofullerenes**

The elements other than carbon that are either on the network or on the inside of the cage should affect electronic structures of the resulting molecules. Since the electronegativity of doped elements is different from that of carbon, a charge redistribution usually occurs, so does the bond rearrangement. However, as it will be shown below, these rearrangements are localized near the invasion site or on the atoms that near the endohedral metal atom. The rest of the cage remains as the same as that of an isolated fullerene. This is different from fullerite anions in which whole molecule experiences a dramatic change when an electron is added [4.35].

4. 2. 3. 1  

**Sc@C\textsubscript{60} : The bonding between metal and the cage**

In this section, the bonding structure of Sc@C\textsubscript{60} was studied in order to achieve a general understanding of metal-fullerene interactions. Its optimized equilibrium geometry, the charge transfer, displacement of Sc off the C\textsubscript{60} center, the geometrical distortion and the distances between Sc and carbon atom are predicted and results will be discussed.

In Table 4.6, the electronic states, the off-center position of Sc at their equilibrium geometry, the symmetry, the charges on Sc, the total energies, and orbital energies of each electronic state are given. Also given in Table 4.6 are
the percentages of Sc orbital contributing to the HOMO of Sc@C₆₀. We predict that \(4A_1\) state, which is not subject to the Jahn-Teller distortion, is the electronic ground state of Sc@C₆₀ and Sc is off the center by 1.175 Å at its equilibrium geometry. The other two states studied here are subject to the Jahn-Teller distortion. From the experience of our early works on Ca@C₆₀, the Jahn-Teller distortions for the two states are believed to be very small (about 0.05 Hartrees).

The charge transfer from Sc to C₆₀ at its equilibrium position is 2.40 (in which \(s\) electrons lost 1.99, \(p\) electrons lost 0.19, and \(d\) electrons lost 0.22). As indicated by the Mulliken population analysis, the 4s² are all transferred to C₆₀.

Table 4.6. Theoretical Predictions of total energies and charge transfers of different states at their equilibrium structures of Sc@C₆₀.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>(\Delta R)</th>
<th>Sym</th>
<th>Charge</th>
<th>Total Energy</th>
<th>Orbital Energy</th>
<th>Percentage of Sc</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4A_1(a_1^1e_1^2))</td>
<td>2.230</td>
<td>C₅ᵥ</td>
<td>+2.40</td>
<td>-3028.83095</td>
<td>-0.394</td>
<td>-0.191</td>
</tr>
<tr>
<td>(2E_1(a_1^1e_1^1))</td>
<td>2.798</td>
<td>C₅ᵥ</td>
<td>+2.15</td>
<td>-3028.77980</td>
<td>-0.205</td>
<td>-0.201</td>
</tr>
<tr>
<td>(4E_1(a_1^0e_1^3))</td>
<td>2.766</td>
<td>C₅ᵥ</td>
<td>+2.22</td>
<td>-3028.74936</td>
<td>-----</td>
<td>-0.123</td>
</tr>
<tr>
<td>(4A_1(a_1^1e_1^2))</td>
<td>0.0</td>
<td>C₅ᵥ</td>
<td>+3.02</td>
<td>-3028.78832</td>
<td>-0.514</td>
<td>-0.178</td>
</tr>
<tr>
<td>(4A_1(a_1^1e_1^2))</td>
<td>0.0</td>
<td>C₅ᵥ</td>
<td>+2.54</td>
<td>-3028.81193</td>
<td>-0.172</td>
<td>-0.264</td>
</tr>
</tbody>
</table>

a) \(p, d\) functions added to the Wachters basis set of Sc.

b) Sc is at the center of the cage in the same geometry as in case a).

c) Sc is at the center and geometry is optimized.

cage. There is some overlapping between 3d\(^1\) of Sc and the carbon atoms that are close to the Sc atom. As shown in Table 4.6, the charge transfer from Sc to
$C_{60}$ is almost +3 when the Sc atom is moved to the center of $C_{60}$ and no geometry optimization procedure has been pursued. This charge transfer decrease to +2.54 when the geometry is optimized. So the results of Mulliken population analysis are sensitive to the geometry in this case. The decrease in charge transfer is because the overlap between Sc $3d$, $4d$ and $5d$ and HOMO of $C_{60}$ increase from zero to 0.1 when Sc is moved from center to the off-center positions. There is no $5d$ population if the Sc is at the center.

The last two columns in Table 4.6 show that the mixings of orbital of Sc and $C_{60}$ in the HOMO of Sc@$C_{60}$ are small. The reason for this may result from that the $3d$ orbital of the Sc is not close to any one of the carbon atoms so that no single covalent bond can be formed between Sc and carbon atom since the shortest distance between Sc and C is 2.487 Å (see below). So the percentage of covalent bond is small.

Not shown in Table 4.6 are the results of $^4A_1$ electronic state in $C_{3v}$ symmetry. In some cases the ground state may be obtained in $C_{3v}$ symmetry simply because M would like to bond to a hexagon rather than a pentagon[19]. The energy of optimized geometry of Sc@$C_{60}$ in $C_{3v}$ symmetry is found to be 1.1 eV higher than that in $C_{5v}$ symmetry.

In Table 4.7, we present the symmetry-independent bond lengths of $^4A_1$ and $^2E_1$ states. The distances between Sc and the symmetry-independent carbon atoms are also listed in the Table 2. The charges on carbon are listed in the parentheses. It is worth noticing that the resonance energy in the hexagons
next to the top pentagon that is the closest to Sc increases as the Sc approaches to one end of C_{60}, indicated by the decrease in the differences

Table 4.7 Bond lengths of $4A_1$ and $2E_1$ states at their equilibrium of Sc@C_{60} in C_{5v} symmetry.

<table>
<thead>
<tr>
<th>Atomic Index(i-j)</th>
<th>d</th>
<th>$\Delta d$</th>
<th>R(C(i)-Sc)$^d$ (Å)</th>
<th>Bond</th>
<th>$\Delta d$</th>
<th>R(C(i)-Sc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(32)-C(60)</td>
<td>1.370</td>
<td>+0.002</td>
<td>4.456(-0.0055)</td>
<td>1.373</td>
<td>+0.005</td>
<td>4.713</td>
</tr>
<tr>
<td>C(6) -C(34)</td>
<td>1.374</td>
<td>+0.006</td>
<td>3.529(-0.0375)</td>
<td>1.391</td>
<td>+0.023</td>
<td>3.585</td>
</tr>
<tr>
<td>C(31)-C(53)</td>
<td>1.378</td>
<td>+0.010</td>
<td>4.257(-0.0145)</td>
<td>1.369</td>
<td>+0.001</td>
<td>4.462</td>
</tr>
<tr>
<td>C(8) -C(15)</td>
<td>1.396</td>
<td>+0.028</td>
<td>3.097(-0.0574)</td>
<td>1.382</td>
<td>+0.014</td>
<td>3.025</td>
</tr>
<tr>
<td>C(1) -C(24)</td>
<td>1.416</td>
<td>+0.046</td>
<td>2.487(-0.1171)</td>
<td>1.409</td>
<td>+0.041</td>
<td>2.303</td>
</tr>
<tr>
<td>C(9) -C(8)</td>
<td>1.438</td>
<td>-0.013</td>
<td>2.796(-0.0854)</td>
<td>1.452</td>
<td>+0.001</td>
<td>2.627</td>
</tr>
<tr>
<td>C(31)-C(35)</td>
<td>1.440</td>
<td>-0.011</td>
<td></td>
<td>1.458</td>
<td>+0.007</td>
<td></td>
</tr>
<tr>
<td>C(6) -C(10)</td>
<td>1.447</td>
<td>-0.004</td>
<td></td>
<td>1.435</td>
<td>-0.016</td>
<td></td>
</tr>
<tr>
<td>C(1) -C(2)</td>
<td>1.449</td>
<td>-0.002</td>
<td></td>
<td>1.463</td>
<td>+0.012</td>
<td></td>
</tr>
<tr>
<td>C(56)-C(57)</td>
<td>1.451</td>
<td>+0.000</td>
<td>4.463(-0.0097)</td>
<td>1.447</td>
<td>-0.004</td>
<td>4.954</td>
</tr>
<tr>
<td>C(32)-C(31)</td>
<td>1.451</td>
<td>+0.000</td>
<td></td>
<td>1.447</td>
<td>-0.004</td>
<td></td>
</tr>
<tr>
<td>C(6) -C(7)</td>
<td>1.454</td>
<td>+0.003</td>
<td></td>
<td>1.442</td>
<td>-0.006</td>
<td></td>
</tr>
<tr>
<td>C(34)-C(35)</td>
<td>1.458</td>
<td>+0.007</td>
<td>3.901(-0.0220)</td>
<td>1.424</td>
<td>-0.027</td>
<td>4.051</td>
</tr>
<tr>
<td>$\Delta R$(Sc-center)</td>
<td></td>
<td></td>
<td>1.175</td>
<td></td>
<td></td>
<td>1.481</td>
</tr>
</tbody>
</table>

All bond lengths and distances are in Å.

a) Charges on C(i) are shown in the parentheses following the R(C(i)-Sc).

of three bond lengths characterizing the hexagons. This is one of the reason Sc moves away from the center so that it can bond to a carbon network to lower the total energy. It is a little surprising that the C-C bond lengths in the top pentagon do not change at all even though the distances between these carbon atoms and Sc are the shortest ones. This can be explained because the antibonding orbital of these bonds are farther away from the Sc atom than the double-bonds attached to the top pentagon.
The other important fact needs to be pointed out in Table 4.7 is that almost two-thirds of the C-C bond lengths in Sc@C_{60} do not change comparing with that of a perfect C_{60}. So the bonding between Sc and C_{60} disturbs only a small part of C_{60} network. It is obvious that if the cage is large enough, many Sc atoms can bond to the cage without knowing the existence of each other because of the small size of Sc atom/ion unless they are bounded together.

Also shown in Table 4.7 is a good correlation between the Sc-C distances and the charges on carbon predicted by the Mulliken population analysis. The distances between Sc and C vary from 2.487 Å to 4.463 Å in $^4A_1$ state. The corresponding charges on these carbon atoms are from -0.1171 to -0.0055. As a result of the non-uniformly distributed charges, the carbon cage has a dipole moment arisen from the charge transfer but should be very small since the position of Sc(+2.40) and the center of the negative charges is very close. The predicted first order dipole moment created by the above charge displacement is only 0.077 a.u.. On the other hand, the estimated dipole moment based on the uniformly distributed negative charges on C_{60} cage and Sc would be 5.52 a.u..

The energy surface of Sc@C_{60} versus the position of the Sc atom is shown in Fig. 4.6. As we can see, the potential curvatures of both energy minimums are quite large. The transition state is where Sc is at 0.5 Å off the center of C_{60} cage. If no geometry optimization is involved, the barrier could be as high as 1.34 eV. By adopting the pseudo-geometry optimization mentioned earlier, the barriers are found to be only 0.65 eV and 0.14 eV for two directions.
We should mention that the binding energy of Sc@C_{60} compares to Sc and C_{60} is predicted to +1.1 eV (unbounded) according to current method.

Fig. 4.6 Total energy as Sc moves along the C_{2v} axis in C_{60}

Since SCF-HF method usually underestimates the binding energy, we think that the binding energy can be close to zero or even negative is local density theory is employed. Interestingly, the above value is smaller than that of Ca@C_{60}, which is +1.3 eV at the same level of theory.
bond and charge rearrangement in Na@C_{59}B and C_{59}BN

Other ways of derivatizing C_{60} include forming doped fullerenes and doped endohedral fullerenes. The assembly of these molecules is also dependent on the valence structures of the elements. In the following, an interesting proposal of making an endohedral doped fullerene is considered. For the proposed molecule, the charge transferred from the endohedral atom will passivate the electron-deficient doping element in the cage. Since the transferred electrons are balanced by the doping elements, the cage will not be electron rich.

Since the total number of the valence electron in Na@C_{59}B is the same as that in C_{60}, it is expected that Na@C_{59}B should be as stable as C_{60}. In fact, the large HOMO-LUMO gap and high ionization potential predicted in this work are in consistent with the expectations. The results of the predicted electronic ground state, the total energies, the HOMO-LUMO gaps, ionization potentials (IP), and the results of Mulliken population analysis of Na@C_{59}B are shown in Table 4.8. The HOMO-LUMO gap of Na@C_{59}B is 7.5 eV compared to 7.8 eV of C_{60}; and the IP of Na@C_{59}B is 7.5 eV compared to 8.5 eV of C_{60}. So Na@C_{59}B seems to be a chemically stable molecule since it has similar quantities as C_{60}. On the other hand, as it is shown in Table 1, there is still a large portion of positive charge possessed by the boron atom, resulting from the difference in the electronegativities between boron and carbon atoms. Hence the boron site is still
somewhat reactive. However, the carbon atoms 2, 5, and 24 surrounding the boron atom also contain most of the negative charge. This negative charge could offset most of the positive charge on the boron atom as the reactants

Table 4.8 SCF-HF predictions of ground states, total energies, HOMO-LUMO gaps, ionization potentials (IP), and charges of Ca@C₅₅B, Na@C₅₅B, (C₅₉B), and C₅₉BH a)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>Total Energy</th>
<th>HOMO/LUMO</th>
<th>IP (eV)</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca@C₅₅B</td>
<td>²A'</td>
<td>-2932.50962</td>
<td>0.292 b)</td>
<td>4.9</td>
<td>B: +0.48</td>
</tr>
<tr>
<td>Na@C₅₅B</td>
<td>¹A'</td>
<td>-2417.86896</td>
<td>-0.275/-0.031</td>
<td>7.5</td>
<td>B: +0.63</td>
</tr>
<tr>
<td>Na₅₅B</td>
<td>¹A'</td>
<td>-2417.86720</td>
<td>-0.253/-0.012</td>
<td>6.9</td>
<td>B: +0.63</td>
</tr>
<tr>
<td>C₅₉BN</td>
<td>¹A'</td>
<td>-2272.64156</td>
<td>-0.293/-0.024</td>
<td>8.0</td>
<td>B: +0.80</td>
</tr>
<tr>
<td>C₅₉B</td>
<td>²A'</td>
<td>-2255.92760</td>
<td>-0.266/-0.025</td>
<td>7.2</td>
<td>B: +0.63</td>
</tr>
<tr>
<td>C₅₉BH</td>
<td>¹A'</td>
<td>-2256.54705</td>
<td>-0.299/-0.051</td>
<td>8.1</td>
<td>B: +0.56</td>
</tr>
<tr>
<td>C₆₀</td>
<td>¹A₁</td>
<td>-2269.14567</td>
<td>-0.304/-0.023</td>
<td>8.3</td>
<td></td>
</tr>
</tbody>
</table>

a) The units of total energy and HOMO/LUMO gap are in hartrees.
b) The HOMO-1 closed molecular orbital.
c) The charges on C surrounded the boron atom are given. The first entry is for C(2) and C(5), which are equivalent. The second entry is for C(24).

approach the Na@C₅₅B from a distance. As a result of it, the boron atom in Na@C₅₅B remains electron-deficient but is a much less reactive site than that in C₅₉B. The results presented above reveal some special properties a large
molecule such as NaC$_{59}$B could have: even though it is a molecule with high IP and large HOMO-LUMO gap, it still could be electron deficient locally. The other species being studied is C$_{59}$BN. It has a HOMO/LUMO gap almost as large as that of C$_{60}$. However, the charges on B and N atoms are large too. They are also surrounded by carbon atoms that have opposite charges on them. But apparently the net charge on both B and N is higher than that on B atom in Na@C$_{59}$B. It seems that this could be a stable molecule if B and N sites can be passivated.

Other possibilities to further passivate the boron site by adding more electrons to the cage and hydrogen attachment to the boron atom has also been explored. As an example, Ca@C$_{59}$B is studied in this work and the results are also given in Table 4.8. It is worth noticing that the boron atom in Ca@C$_{59}$B still possesses a +0.48 charge even though two 4s electrons of Ca have been transferred from calcium to the cage. However, the decreased positive charge on B together with the unchanged negative charge on the carbon atoms surrounded the boron atom make Ca@C$_{59}$B to be much less susceptible to the attack from Lewis base. The hydrogen attachment results in C$_{59}$BH, which has one hydrogen attached to the boron atom. Since the boron site is protected by the hydrogen atom and the HOMO-LUMO gap is large (even larger than that of Na@C$_{59}$B), this molecule should be a very interesting target for isolation.

Part of the geometric arrangements of the molecules predicted in the work is presented in Table 4.9. It is found that the B-C bond lengths are about 0.1 Å
longer than their C-C counterpart in C_{60}. The increase in the bond length is limited to the three bonds around the boron atom.

The predicted relative locations of the Na and the Ca atoms inside the C_{59}B cage are given in Table 4.9, which are both 0.900 Å away from the center. It should be pointed out that both positive charged Na and Ca nuclei locate closely to the boron atom that also has positive charge rather than on the center axis passing through a pentagon or a hexagon as other metal atom did in the endohedral metallofullerenes [4.36]. This result was confirmed by applying C_{7} symmetry to the molecules. It was therefore found that Na was located closely to the boron atom and on the axis that pass through the center of the triangle formed by three carbon atoms (2, 5, and 24) surrounded the boron atom. (C_{5} symmetry was then used to further optimize the geometry). The cause of this can be understood by estimating the collective electrostatic forces exerted on the Na atom by all the atoms in cage. Because the negative charges are also concentrated on the carbon atoms around the boron atom, and the distance

<table>
<thead>
<tr>
<th>Molecule</th>
<th>B - C(24)</th>
<th>B - C(2)</th>
<th>B - C(5)</th>
<th>B - M (H)</th>
<th>M - Center</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca@C_{59}B</td>
<td>1.486</td>
<td>1.563</td>
<td>1.563</td>
<td>2.899</td>
<td>0.890</td>
</tr>
<tr>
<td>Na@C_{59}B</td>
<td>1.484</td>
<td>1.558</td>
<td>1.558</td>
<td>2.847</td>
<td>0.900</td>
</tr>
<tr>
<td>C_{59}B</td>
<td>1.490</td>
<td>1.548</td>
<td>1.548</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>C_{60}</td>
<td>1.368</td>
<td>1.451</td>
<td>1.451</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>(C_{59}B)H</td>
<td>1.585</td>
<td>1.610</td>
<td>1.610</td>
<td>1.203</td>
<td>-----------</td>
</tr>
</tbody>
</table>
between Na and these carbon atoms are shorter than that from Na to B, the Na is pulled to the side where the boron atom stays.

The estimated binding energy of Na@C_{59}B compared to Na and C_{59}B is 3.9 eV. Since no covalent bonding was found between Na and the cage, this large binding energy originates solely from the coulomb interaction between the Na cation and the negatively charged cage. Another interesting result is that when Na is put on the outside of the cage next to the boron atom, the binding energy of the resulted exohedral NaC_{59}B is very close to the one the endohedral molecule has. The major difference comes from the HOMO-LUMO gap and IP value, as shown in Table 4.8.

Since the first experiment on the doped fullerenes reported three years ago, many studies have been carried out on C\textsubscript{n}X\textsubscript{m} (X = B, N) systems [4.37-4.39]. It was found that the charge on the boron atom in C_{59}B was +0.5 employing the molecular orbital method [4.37]. The corresponding bond lengths are from 1.49 Å to 1.56 Å. In other studies, the carbonanes bond length is longer than 1.500 Å [4.38, 4.39]. So the results presented in this work are in general agreement with other predictions on the charges and bond lengths for the similar systems.

4.2.4 Sc\textsubscript{8}B\textsubscript{12}: A Stable Molecule with a Closed-Shell Ground State
Another fascinating property of carbon is that it can form many stable compounds with transition metals by taking interstitial positions in metal clusters and in bulk metals. Other element, like boron and nitrogen, form similar structures with transition metals. Since the first met-car Ti₈C₁₂ was found in the gas phase [4.40], a few other metal elements substituted met-car systems had also been found [4.41]. Original speculations and later theoretical calculations both suggested the significant role of the d electrons in the metal atoms play in the chemical bonding between metal atoms and carbon atoms [4.42]. The significance of the carbon atoms is suspected to be that they can form different orders of the covalent bonds among themselves and with metal atoms [4.43].

Since Ti₈C₁₂ has an open-shell electric ground state and is very reactive, other systems with high stability are worth to be explored. The criterion of the stability of the molecules under investigation is the binding energy of the molecule. In the following, we found that Sc₈B₁₂ is a stable molecule with closed electronic ground state. The closed-shell property is very important since the applications of these met-car molecules will very much depend on their availability. With a closed-shell molecule, it will be much easier to isolate them.

Using both ab initio SCF-HF method and single point density functional theory energy calculation, we predict that Sc₈B₁₂ has a closed-shell electronic ground state and high atomization energy comparable to that of the newly discovered met-car Ti₈C₁₂ (which has an open-shell ground state ⁶A₉). The atomization energy of Sc₈B₁₂ in this study is 2.27 eV/atom compare to 1.56
eV/atom for that of Ti\textsubscript{8}C\textsubscript{12}, and the HOMO-LUMO gap for Sc\textsubscript{8}B\textsubscript{12} is about 7.2 eV. The current calculations indicate that Sc\textsubscript{8}B\textsubscript{12} may be produced in the macroscopic amount in the lab, and if so, it should be isolated much easier than Ti\textsubscript{8}C\textsubscript{12}.

Table 4.10 SCF-HF predictions on M\textsubscript{8}X\textsubscript{12}.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Total Energy</th>
<th>Eb (eV)</th>
<th>LUMO</th>
<th>HOMO</th>
<th>\Delta E(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti\textsubscript{8}B\textsubscript{12}</td>
<td>-7081.85052</td>
<td>21.5</td>
<td>-0.137(a\textsubscript{u})</td>
<td>+0.004(e\textsubscript{u})</td>
<td>3.8</td>
</tr>
<tr>
<td>Ti\textsubscript{8}C\textsubscript{12}</td>
<td>-7239.79227</td>
<td>31.2</td>
<td>-0.152(3t\textsubscript{g})</td>
<td>-0.165(1a\textsubscript{u})</td>
<td>0</td>
</tr>
<tr>
<td>Ti\textsubscript{8}N\textsubscript{12}</td>
<td>-7439.55252</td>
<td>6.2</td>
<td>-0.178(t\textsubscript{u})</td>
<td>-0.031(t\textsubscript{g})</td>
<td>3.6</td>
</tr>
<tr>
<td>Sc\textsubscript{8}B\textsubscript{12}</td>
<td>-6373.56775</td>
<td>45.3</td>
<td>-0.242(t\textsubscript{u})</td>
<td>+0.024(t\textsubscript{g})</td>
<td>7.2</td>
</tr>
<tr>
<td>V\textsubscript{8}B\textsubscript{12}</td>
<td>-7836.21858</td>
<td>7.0</td>
<td>-0.192(t\textsubscript{u})</td>
<td>+0.010(t\textsubscript{g})</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 4.10 lists the molecules and their properties under investigation. All the molecules are studied in T\textsubscript{h} symmetry. Since the binding energy is a critical factor to decide the stability of the molecules, we first present the calculated binding energies of the molecules. It is shown in Table 4.10 that Sc\textsubscript{8}B\textsubscript{12} has the highest SCF-HF binding energy of 45 eV among all the molecules studied here. That is even higher than the binding energy of Ti\textsubscript{8}C\textsubscript{12}. The results from a higher level of calculation including electron correlation on these molecules are presented in Table 4.11. It shows that binding energy of Ti\textsubscript{8}C\textsubscript{12} is actually 20% higher than that of Sc\textsubscript{8}B\textsubscript{12}.

It is well known that SCF-HF method always underestimates the dissociation energy and local density method usually overestimate them. Hence
the binding energy of Sc₈B₁₂ may be close but less than that of Ti₈C₁₂, but former has a closed shell ground state.

C₂ᵥ symmetry was also used to predict the ground state of Sc₈B₁₂. It shows that Sc₈B₁₂ possesses a nearly T₄ symmetry and only slightly improvement in total energy has been found.

Table 4.11  BLYP energy of M₈X₁₂

<table>
<thead>
<tr>
<th>Molecules</th>
<th>BLYP</th>
<th>Eb(eV)</th>
<th>X-X</th>
<th>X-M</th>
<th>M-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₈C₁₂</td>
<td>-7251.63687</td>
<td>-93.1</td>
<td>1.438</td>
<td>1.982</td>
<td></td>
</tr>
<tr>
<td>Sc₈B₁₂</td>
<td>-6383.00043</td>
<td>-69.1</td>
<td>1.497</td>
<td>2.326</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.11 also gives the bond length of M-M, M-X, and X-X from SCF-HF method. The bond length calculated by SCF-HF method is very close to that found by using density functional theory [4.44]. For example, the Ti-C bond is calculated to be 1.980Å in this paper and is 1.970Å with DFM. This means that although single configuration SCF-HF method may not predict precisely the total energy when state density close to the Fermi level is very high, it can still predict the equilibrium geometry with reliable accuracy.

4.3 Electronegativity and the growth of metallofullerenes

The effect of metal on the formation of endohedral metallofullerenes can be generalized if the electronegativity of the elements are considered. It has
shown that electronegativity, hardness, ionization potential, and electron affinity can be calculated if two of them are known [4.45]. Therefore, IP or EA along cannot determine the ionicity of chemical bonds. This is corroborated by the fact that Al has not yet been found to form endohedral fullerenes even it has IP of 6.0 eV.

Fig. 4.7 shows the correlation between the electronegativity [4.46] of elements and its success of becoming an endohedral metallofullerene. The

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Fig. 4.7 Electronegativity and the endohedral metallofullerenes
physical meaning behind this picture is that the bonding structures between metals and fullerene precursors, which determines whether the metals can be trapped or not, are controlled by the difference in their electronegativities. Since carbon condenses at much higher temperature than do the regular metals, fullerene precursors that consist of almost annealed forms of fullerenes will react with metal atoms. If the electronegativity of metals is comparable to that of carbon, covalent bonds will form and metal elements become embedded in the cage. If a charge-transfer complex is formed between metal and fullerene precursor, the interaction between them will lead the metal ion into the cage before the latter is closed.
Chapter 5 Growth models for the self-assembled carbon nanotubes

The fullerene nanotubes produced in the DC arc discharge in 1991 [5.1] have signified another surge of carbon research after the synthesis of macroscopic quantity of fullerenes in 1990 [5.2]. It has also challenged the current theory since carbon alone is not supposed to warrant such tubular structures. Growth mechanisms involved electric field/field emission stabilization [5.3] and hydrogen saturated dangling bonds [5.4] have so far been proposed to account for the formation of tubes formed in DC arc discharge and in hydrogen environment.

Recently, we have observed multi-walled nanotubes in a laser vaporization environment that has neither electric field nor hydrogen at present [5.5]. Hence the electric field and hydrogen play no roles in assisting the growth of multi-walled nanotubes in this case. What could be the intrinsic force that helps carbon form such a multi-walled tubular structure? In section 5.1, we present a model that involves a new concept, lip-lip interaction, to rationalize the growth of multi-walled tubes in the laser vaporization environment.

Another new phenomenon we have observed is that when metals that usually could not be trapped into fullerene cages are vaporized by a laser light, single-walled carbon nanotubes (SWTs) are produced [5.6]. This new morphology of carbon has not yet been observed when no metal is present. One
may visualize this structure as fullerenes of extremely large aspect ratio, a parameter measuring the length to diameter ratio, of 10 to 1000. These objects have been calculated not as stable as round fullerenes of the same size [5.7]. The growth of SWTs is less favored than fullerene onions and since there is no double layer, the lip-lip stabilization does not happen either. Hence a new growth model of SWTs is presented in 5.2 based upon the studies the plasma history and the interactions between carbon and metal atoms/clusters. Since the involvement of metal is vital to the formation of SWTs, the process of growing SWTs becomes the intrinsic property of the mixtures, or the combination of the self-assembling ability of carbon and the catalytic properties of metal nano particles.

5.1 Growth of multiple-walled carbon nanotubes: Lip-Lip interactions

The three well-known forms of carbon are graphite, fullerenes and diamond [5.8]. Graphite possesses a stacked planar structure with each plane consisted of hexagonal network of carbon atoms. Diamond had a totally different structure in which each carbon is surrounded by and covalently bonded with four equally distant carbon neighbors. In other words, carbon atoms in graphite are in $sp^2$ hybridization and in $sp^3$ for carbon in diamond. Amorphous carbon has both bonding structures, that is, it consists of carbons that either has three neighbors or four neighbors that are all about 1.4 Å apart. Carbon atoms in fullerenes
mainly undertake $sp^2$ hybridization and are more resemble to that of graphite than diamond. This is partly due to that fullerene form is the globe minimum on the potential energy surface formed by a limited number of carbon atoms at high temperature of about 2000 to 2500 K [5.9], the condition under which carbon usually stays as graphite. When the number of carbon atoms increases, large fullerenes and onions form and eventually, graphite, excluding the possibility of the growth of both multi-walled or single-walled nanotubes.

In DC arc discharge, when the temperature is higher than 2500 K and there is an electric field present around the growth region, rate of the closure of open fullerenes precursors is slowed down since the open edges are stabilized by the electric field in the region across the cathodic sheath [5.10].

The laser vaporization environment is different. As the nanosecond laser light pulse reaches the graphite surface, all the chemistry happens in the first 10-100 $\mu$s [5.11] since carbon density and the temperature of the plasma generated by laser pulse both drop to minimal after this period of time. Due to the high yield of fullerenes produced by this technique, it is reasonable to assume that there should be a lot of fullerene precursors, which are the unclosed forms of fullerenes. These precursors drift around in space for certain time and most of them will collide with small carbon clusters to close its open end and become fullerenes. It turns out that this form of carbon precursors at those specific time intervals is the crucial to the gas phase self-assembly of multi-walled fullerene nanotubes.
By increasing the carbon density and so the density of precursors, the possibility of the collisions between two precursors increases. The collision with *correct orientations* between two precursors so that one lies on the top of another, as shown in the lower branch of Fig. 5.1, leads to a special kind of interactions, lip-lip interaction, that stabilizes the open end for some moment and thus prevents the structure from closing. We therefore refer this open-end-double-layer-bowl-shaped carbon network as a tube precursor. Since carbon density is relative high at this stage as well as the temperature, the reaction of adding more carbon feedstock to this tube precursor proceeds and the tube keeps growing until the carbon density is too low or the open tube closes. The tube precursor is similar to amorphous carbon in terms of bonding definition, with a mixing of $sp^2$ and $sp^3$ hybridization.

Fig. 5.1 Multi-walled carbon nanotubes grown by lip-lip interaction
From above discussions, it is obvious that a high carbon density or fast rate of supplying the carbon feedstock is crucial to the growth of tubular structures. If enough time is given to the tubular precursors they will be annealed into onion of concentric fullerenes since the latter are the energetically favored structures [5.7]. For tubes to grow in the gas phase, collision with correct orientations is the crucial factor. Since large pieces of fullerene precursors can only form in the later stage of the plasma, and the feedstock density will not stay high for a long time, it is therefore believed that the possibility of forming long nanotubes in the laser vaporization apparatus is limited. This is very different from the growth of nanotubes in the DC arc discharge in which carbon feedstocks are preserved at high density for a long period of time. Therefore, the length of the resulting nanotubes from DC arc should be longer than that from laser vaporization, as proved by the experimental results that have shown the former are on the order of 5-50 μm and the latter 0.3 μm [5.12].

5.2 Growth of single-walled nanotubes

The studies of the interactions between metals and carbon/hydrocarbons under different circumstances have greatly expended our knowledge on catalytic chemistry in the last four decades. Catalysis of graphitization (conversion from
disordered structures of carbon into graphite) [5.13], hydrogenolysis and dehydrogenation [5.14], fabrication of carbon fibers and filaments consisted of multiple cylindrical carbon layers with inner diameters from 5 to 1000 nm [5.15], and synthetic diamond [5.16] are a few among many examples. These catalytic processes all occurred on the well-characterized surface of metal crystals or finite particles. The mechanisms that govern the above processes have been mostly comprehended although some of the arguments are still under scrutiny [5.17].

Recently, single-walled carbon nanotubes with inner diameters of 0.6-6 nm has been discovered in the soot made by DC arc discharge between a graphite cathode and an anode filled with metals or their oxides [5.18]. The understanding on the growth of those SWTs has been very limited although much work has been done on the production of SWTs. As it will be shown in the following, similar tubes with less amorphous carbon covered on them can also be produced by direct laser vaporization of metal-graphite composite targets. Since this later technique also provides a good control over the growth conditions as it has been demonstrated in the study of the growth of fullerenes [5.19], it is used to investigate the growth mechanism of SWTs in a catalytic environment.

The results given in section 3.5.2 reveal several important facts: (1) the annealing condition (most importantly the temperature) in which fullerenes are produced in high yield has to be approached to produce high yield SWTs
although different metals prefer different ranges of it. Therefore, a high yield of SWTs can only be achieved when that of fullerenes is not too low. It indicates that annealing tubes is probably easier than fullerenes because of the presence of metal particles. (2) since that almost all the metals, including Pt, Cu, and Ti, can catalyze graphitization, the annealing condition will not necessarily warrant the formation of SWTs for fullerenes can redissolve in giant metal particles and reprecipitate out as graphite [5.13]; therefore, particles of size on the order of nanometer are definitely required for the formation of SWTs. When these metal particles aggregate into large ones, the catalytic processes caused the growth of SWTs slow down, and at certain point, they are replaced by that of graphitization. This also explains why no correlation has ever been found between size and location of SWTs and large catalytic particles. (3) the difference among metal themselves reveals that metal-carbon interactions affect the growth of SWTs. The interactions or bonds between metal and carbon should not be too strong or too weak so that carbon can not only easily chemisorb onto and but also easily departure from metals. A good catalyst should be able to rupture the carbon-carbon bonds in amorphous carbon and catalyze the formation of aromatic rings in a high rate. Pt/Co is a better catalyst than Co in this sense because Pt is known to be a good catalyst in the conversion of alkanes/cycloalkanes into cycloalkanes/aromatics, in addition to the fact that Pt/Co has a lower melting point than that of Co [5.20]. (4) The range of temperature within which SWTs can be produced also depends on the metals.
It should be pointed out that this effect is not only determined by the melting points of metals or metal alloys that affects the carbon diffusivity, it is also affected by the type of reactions happening on the metal surface: endothermic reactions prefer high temperature and exothermic low temperature. The formation since the surface diffusivity also depends on the temperature. The general trend of temperature effect is that for some metals, the yields of SWTs seem less sensitive to temperature than that of fullerene; others have the reverse trend, such as Ni. This indicates that melting point argument alone is not enough to explain the experimental results [5.21].

Considering the four observations listed above, a growth model is constructed, which is shown in Fig. 5.2. Carbon atoms produced by laser vaporization first condense into carbon chains and rings followed by the reaction with metal vapors (stays as vapor at above 2500 K). As the clusters growing, more metal atoms are incorporated. Since transition metals prefer high connectivity structures, metal atoms in these carbon clusters intend to aggregate into metal clusters for solely energetic reasons [5.22]. Therefore, metal-carbon binary clusters at this stage have structures of which metal or metal carbide takes one end and carbon clusters the other. The large number of carbon atoms on one side should transform or being annealed into fullerene shapes at such a high temperature. Metal may also assist the formation of fullerene precursors at this temperature since the linear chain to aromatic ring conversion is an endothermic process. Hence, metal clusters with fullerene tails form as the
precursors of SWTs. Meanwhile, amorphous carbon, when contact with those metal clusters, can be transformed and transported easily from one side of them to the fullerene side due to the concentration gradient of carbon in them. The break of carbon-carbon bond in amorphous carbon on metal surface is an exothermic reaction and that also help that end of the cluster takes more carbon.

![Diagram](image)

**Fig. 5.2** Growth model for the SWTs

The high rate of transportation is facilitated by (1) the high bulk and surface diffusivity of carbon because of the melting temperatures of these small clusters could be very low; and (2) metal-carbon bonds are not too strong in these metals so that can precipitate out easily. The high percentage of surface atoms (>75%) in these small metal clusters (~1 nm) makes themselves very reactive toward amorphous carbon feedstocks. Therefore, SWTs grow in a high speed on one
end driven by the difference in the Gibbs free energies between SWTs and the feedstocks. Lowering temperature will decrease the diffusivity of carbon across the clusters and slows down the process of linear chain to aromatic ring conversion.

Since the carbon density when SWTs are produced is similar to that when high yield fullerene are synthesized, which is about 4 time less than that when multi-walled nanotubes are fabricated, it is not high enough to have the second layer overcoated on the outside of the SWTs. Other factors preventing this from happening include the small curvature of SWTs and the resulted small sticking probability of these small species to the surface.

It should also be emphasized that the SWTs made by the laser-furnace are almost free of amorphous carbon covering on them. This result can be explained because of high yield of SWTs and better annealing conditions for both SWTs and fullerenes, particularly the SWTs, and a better annealed SWT is much less reactive and hard to stick on for amorphous carbon.

High yields of SWTs can also be produced by vaporizing mixtures of two or more metals, such as Fe/Co, Ni/Co, Pt/Co etc. Since a binary alloy usually has a lower melting point than that of each metal consisted the alloy, the reason that alloy produces more SWTs may simply rely on the fact that lower melting point of the alloy facilitates the transportation of carbon in it [5.21]. On the other hand, the lowering of melting point of a binary metal alloy is quite small, at about 5%. This can hardly explain the hundredfold increase in the yield. Cu does not
help Co in catalyzing more SWTs when Cu/Co alloy is used. This may be due to surface segregation of Cu since it is not a good catalyst for the formation of SWTs or graphite. Other effects such as the increased activities and selectivity of these alloys as discussed above may be more important although affirmative conclusions for each system demand more theoretical and experimental efforts. The latter may be facilitated by an ultrafast X-ray diffractometer or EXAFS on which the author is about to working in Professor Kent R. Wilson's laboratory.
Chapter 6 Conclusions

Novel materials self-assembled by laser vaporization are studied by the Fourier Transform Ion Cyclotron Resonance (FT-ICR) supersonic cluster beam apparatus and transmission electron microscope (TEM). Based on the experimental results and theoretical studies employed the self-consistent (SCF) Hartree-Fock (HF) method and density functional theory (DFT), the growth mechanisms of metallofullerenes, which is referred as extended isolated pentagon rules (EIPR) that incorporate the interactions between metals and carbon is proposed. Properties of different metallofullerenes, doped fullerenes, and endohedral doped metallofullerenes have also been investigated. Special features of U@C_{28}, Co_{55}, La@C_{82}B, Eu@C_{82}, C_{74}, Y@C_{60} are presented. Carbon nanotubes, its production and growth mechanisms in the laser vaporization environment have been studied in detail. The growth mechanism of single-walled carbon nanotubes denoted as size-limited break-diffusion-formation (SLBDF) has been formulated. A new concept called lip-lip interaction that is crucial to the understanding of the multiple-walled carbon nanotubes has also been invented. The laser-vaporization technique has also been found to be able to produce higher yield and less amorphous carbon covered single-walled nanotubes than DC arc discharges.
References


[1.27] A large barrier should be easily perceived since the conversion between open fullerene sheet and fullerene involved with the transformation between dangling bonds and fused pentagons.


[1.31] T. Guo and R. E. Smalley, to be published


[4.24] Three 4p functions added to Ca


[4.26] The Na and Ca DZ basis sets were taken from the TURBOMOLE library.


[4.34] Geometry of empty fullerenes has been supplied by L. Beaudux in Professor Scuseria's group.


[4.45] Periodic Table of Elements, Sargent-Welch Scientific Company, 1979


