A glimpse into the fascinating world of fullerenes

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Fullerenes, carbon nanotubes and onions have caught the imagination of the entire scientific community. The interest seems to be growing unabated; about two papers per day are being published today. This article sketches the fascinating area of this new allotrope of carbon, maybe the only allotrope of any element discovered in 20th century, focusing primarily on C$_{60}$. The early history, synthesis and characterization, mass spectrometry, derivatization, orientational ordering, pressure effects, superconductivity, magnetism and photophysical properties of fullerenes and fullerene-based compounds will be discussed. The science of buckminsterfullerenes and fullerenes in general, is still dominated by spectroscopy and chemical physics. Although many applications were proposed in the early days of fullerenes, many of them turned out to be disappointments. However, potential uses of fullerene-based materials in photophysical, biological and chemical applications are increasingly recognized.

The role of serendipity in scientific discoveries is widely recognized. The story of buckminsterfullerenes, C$_{60}$ and fullerenes in general, is no exception. Scientists in their fascination to understand the chemistry of interstellar molecules, hit upon an unusual and most extraordinary discovery in the history of chemistry. The molecule they discovered had sixty equivalent carbon atoms which formed the pattern of a football giving it the highest symmetry. Theoretical predictions of such structures were known from 1970. There is no molecule formed by the same atom in chemistry as big as buckminsterfullerene. Elemental carbon has been known for millennia to be occurring in two polymorphic forms, graphite and diamond. Graphite has two dimensional layers of sp$_2$ hybridized carbon atoms interlinked by weak van der Waals forces. Since the inter-layer interaction is weak, graphite is used as a lubricant. Diamond, however, is one of the hardest materials known to man. This property arises from the strong three-dimensional bonding in diamond in which each sp$_3$ hybridized carbon atom is bonded to four other similar atoms. Fullerenes constitute another allotrope of carbon, probably the first allotrope of any element discovered in recent times. Figure 1 shows the structures of graphite, diamond and C$_{60}$. There are also other all-carbon molecules similar to C$_{60}$ with cage structure, collectively called fullerenes in honour of the famous American architect Buckminster Fuller whose geodesic domes are landmarks of 20th century architecture. There are other forms of carbon such as carbon rings which are receiving considerable attention today.

The 1996 Nobel Prize in Chemistry was awarded to Sir Harold Kroto of University of Sussex, UK and Robert Curl and Richard Smalley of Rice University, Houston, Texas, for their work on buckminsterfullerene.

It was only natural for a molecule of such immense beauty to attract the whole of the scientific commu-
nity. The structure, spectroscopy, chemistry, materials science and applications have been intensely investigated. Because of all these, buckminsterfullerene became the subject matter of nine out of ten of the most cited papers in chemistry in 1991. The position improved further in 1992 to make ten out of ten. According to statistics, one paper per week got published in this area from 1985 to 1990. After 1990, it is said do be one per day. In 1995, it was slightly less than two per day.

Molecules with 70, 76, 84 and other numbers of carbon atoms were soon characterized. Developments in 1991 showed that these molecules need not be found only with tens and hundreds of atoms but also with thousands of atoms. These giant molecules of carbon occur as nanometer size tubes and balls which are called carbon nanotubes and onions, respectively. A number of new geometries are proposed in recent research. The chemistry and physics of the new forms of carbon will continue to excite scientists in the coming years.

In this article, I intend to give an account of the chemistry, physics and materials science of this new form of carbon in a rather illustrative fashion. I may not present a balanced view of the subject matter as my own interests in the area are rather limited. There have been numerous conferences on fullerenes and even on specialized topics of fullerene chemistry and physics over the years. Several books on fullerenes have appeared in the recent past and a comprehensive review in the limited space is nothing but impossible.

Discovery and early years

As noted earlier, the search for certain linear molecules of carbon normally found in the interstellar region called cyanopolyynes, was the starting point of this search. Some of these molecules of the type H-C≡C-C≡C-C≡N or HCN have been synthesized in the laboratory. These molecules containing seven, nine and eleven carbons, were detected by radio-astronomy. However, studies of carbon arc have shown the presence of molecules containing as many as 33 carbon atoms. This was the time when Smalley and co-workers in Houston were working with a newly-developed cluster source which used lasers for evaporation, supersonic molecular beam expansion for clustering and photoionization mass spectrometry for detecting the products. Similar studies were also done by Rohlfing et al. in Exxon. Their studies on graphite which preceded those of Smalley and colleagues showed the presence of carbon clusters heavier than C_{32}, but interestingly no odd number cluster was seen. Soon after the beginning of these measurements, it was observed that species such as HCN and HC3N are formed in the reaction of C_{6} (n < 30) with H_{2} and N_{2}. However, the major discovery turned out to be not the detection of cyano polyynes but the unusually abundant species C_{60}, which dominated the mass spectrum under certain clustering conditions. There were other heavier clusters too. It was found that these clusters were particularly unreactive compared to the lower clusters. Reactivity and photofragmentation studies showed that the 60 atom cluster is extremely stable. The observed chemistry could be explained if one assumes the graphic sheet to transform into a hollow chicken-wire cage similar to the domes of Buckminster Fuller. Such a closed cage requires that 12 = 3n + 2n + 1n + 0n - 1n - 2n, where n is the number of k-sided faces. For carbon, the only values of k are 4 and 6, although 7 is also possible as has been detected recently in carbon nanotubes. This means that there should be 12 pentagonal faces and the number of hexagonal faces are arbitrary. In C_{60}, there are 12 pentagonal faces and 20 hexagonal faces. Fullerenes, the class of closed cage molecules, have the general formula C_{60+n+6}. C_{60} has only one chemically distinct carbon atom. However, in C_{70} there are five distinct carbon atoms. In larger fullerenes there is the possibility of isomers and some fullerenes are also chiral. Very recent studies have shown that there are many isomers to some fullerenes than previously thought of. However, because of the isolated pentagon rule (observed generally), which places pentagons separated by hexagons, the number of isomers is limited.

The experimental apparatus used in the discovery of C_{60} is shown in Figure 2. This set-up is now commercially available for the study of a variety of clusters. A rotating disk of graphite is irradiated with a powerful laser to evaporate carbon. As the laser falls on the disk, a stream of helium gas is passed over the disk by releasing a valve. The gas carries the evaporated carbon species with it and during its passage to the nozzle, the species in the vapour undergo clustering. The cluster...
Box 1. Synthesis and purification of fullerenes

For the synthesis of fullerenes all that you need is a welding transformer, a chamber connected to a vacuum pump (even a single stage oil sealed rotary pump is adequate) and some graphite rods. The graphite electrodes are brought in close contact with each other and an arc is struck in an atmosphere of 100–200 Torr of helium or argon. To sustain the arc, a voltage of 20 V (AC or DC) may be necessary. For a graphite rod 6 mm in diameter, about 50–200 A current may be consumed. Generally, spectroscopic pure graphite of high porosity is used so that evaporation rate is high. The soot generated is collected on water-cooled surfaces which could even be the inner walls of the vacuum chamber. After sustaining the arc for several minutes, the vacuum is broken and the soot is collected and soxhlet extracted for about 5–6 hours in toluene or benzene resulting in a dark reddish-brown solution which is a mixture of fullerenes. 20–30% of the soot so collected is soluble, this soluble material is subjected to chromatographic separation\textsuperscript{18}. Over the years, several simple methods have been discovered including the filtration technique over an activated charcoal–silica gel column\textsuperscript{18}. About 80% of the soluble material is C\textsubscript{60}, which can be collected in one pass using toluene as the mobile phase. C\textsubscript{60} can be separated using toluene/o-dichlorobenzene mixture as eluant. Repeated chromatography may be necessary to get pure C\textsubscript{60}. C\textsubscript{60} solution is violet in colour while that of C\textsubscript{70} is reddish-brown. Higher fullerenes C\textsubscript{70}, C\textsubscript{84}, C\textsubscript{96}, etc. require HPLC for purification\textsuperscript{19}. Spectroscopic properties of several of these fullerenes are now known. Normally, preparation of a gram of C\textsubscript{60} requires about 5 hours of work. But many of the higher fullerenes require over 250 hours to make about 1 mg. C\textsubscript{60} and C\textsubscript{70} are now commercially available from several sources. C\textsubscript{60} is about $175$ a gram but C\textsubscript{70} is not yet affordable for synthetic chemists. Therefore, a majority of the studies reported is on C\textsubscript{60}. Fullerenes crystallized from saturated solutions retain solvent molecules and removing them may require long hours of vacuum drying. Crystal growth by vapour transport is an excellent method to grow millimeter size crystals devoid of solvent for sensitive measurements. For solid state spectroscopic measurements, it is better to use evaporated fullerene films in high or ultra high vacuum to avoid solvent contamination. Evaporation is also used as a method of purification as there is substantial difference in the onset of evaporation between C\textsubscript{60} and C\textsubscript{70}. Calixarenes (bowl-shaped macrocycles with hydrophobic cavities) have been used recently\textsuperscript{19} in the purification of fullerenes. See Figure 4 for a schematic procedure of synthesis and purification.

Arc evaporation is not the unique way of making C\textsubscript{60}. Fullerenes have been found in flames\textsuperscript{11}, upon chemical vapour deposition used to produce diamond\textsuperscript{12}, in a $1.85$ billion year old bolide impact crater\textsuperscript{13} as well as from spacecrafts\textsuperscript{14}. It has also been made from diamond\textsuperscript{15}. No one has made it by chemical reactions but such a possibility has excited many organic chemists\textsuperscript{16}. It has been synthesized from camphor recently\textsuperscript{17}. Mass spectrometry has shown that higher clusters of carbons could be formed by laser evaporation of polymers\textsuperscript{18}. Highly unsaturated carbonaceous ring systems upon laser evaporation\textsuperscript{19} produce C\textsubscript{60}. There are several other exotic means of producing C\textsubscript{60}. However, the total synthesis would indeed be a landmark in chemistry; approaches to this have been suggested\textsuperscript{19}.

Synthesis and purification was followed by the characterization of this material by a variety of spectroscopic techniques. The pivotal role played by mass spectrometry in characterizing fullerenes cannot be overemphasized. NMR showing a single line corresponding to the equivalence of the carbon atoms\textsuperscript{20}, single crystal X-ray structure resolving the atomic positions\textsuperscript{21}, characterization by UV/VIS (refs 107, 122), IR and Raman\textsuperscript{13} spectroscopies, etc. soon followed. Predicted electronic structure was confirmed by Hel and Hell photoelectron spectroscopies\textsuperscript{24}.

At the same time, experiments were also done using a Fourier transform ion-cyclotron resonance (FT-ICR) apparatus. In this set of experiments, mass selected cluster ions were subjected to reactions with a variety of gases. C\textsubscript{60} was extremely unreactive to gases such as O\textsubscript{3}, NH\textsubscript{3} and NO. On the contrary, clusters of other elements such as Si showed high reactivity. In fact no evidence was there to show that Si\textsubscript{60} was special. A body of other experimental data was accumulated by the Houston group on the photophysics, photodetachment beam emanating from the nozzle is selected by a skimmer. The clusters are then subjected to mass analysis by time of flight mass spectrometry. Under certain experimental conditions, the mass spectrum was very similar to that reported previously, showing a distribution of even-numbered species. But a variation in the experimental conditions, especially the introduction of the integration cup (see Figure 2), increased the intensity of the sixty atom cluster to such a point that in some experiments only C\textsubscript{60} and C\textsubscript{70} were seen (Figure 3).
and optical spectrum of C_{60}. None of these studies gave any evidence to suspect the proposed structure.

For nearly five years, C_{60} was truly a chemical physicists playground. A large number of theoretical papers got published on the electronic structure\(^\text{16}\), reactivity\(^\text{17}\), magnetism\(^\text{18}\) and a number of other properties of C_{60}. The studies were made easy by the very high symmetry of the proposed structure. In fact a close similarity between the observed peaks in the IR spectrum of an evaporated carbon soot and the theoretical frequencies\(^\text{19}\) made Kratschmer and colleagues\(^\text{20}\) look for C_{60} in the soot. They were working on laboratory-produced carbon soot in order to understand the interstellar spectrum of carbonaceous materials. The soot they obtained after evaporating graphite resistively in an atmosphere of helium contained four bands in the infrared region. The absorption frequencies correlated well with the proposed bands of C_{60}. Application of solvent extraction yielded significant quantities of fullerenes\(^\text{21}\) from the soot and a host of techniques were applied to the characterization of this newly made form of carbon. For a description of the synthetic procedure, see Box 1.

**Mass spectrometry and ion/molecule reactions**

Soon after a method of macroscopic synthesis of C_{60}, several ion/molecule reaction studies were performed\(^\text{22}\).

In the early days, fullerenes were expensive and mass spectrometer was the ideal reaction vessel. C_{60}^- and C_{60}H^+ were produced by chemical ionization (CI) with methane\(^\text{23}\). It was shown that C_{60}^- was 15 times more abundant than C_{60}H^+, consistent with the high electron affinity. Methane CI spectrum showed protonated fullerenes and adducts of fullerenes with C_{6}H_{5}. Collision-induced dissociation of C_{60}^+ in the keV range with helium showed the expected C_{5}^+, C_{56}^+, etc. fragments like in the earlier photofragmentation study. Fragmentation of C_{60} \(^\text{24}\) yielded only C_{n}^2+ not C_{n}^+ in contrast to polycyclic aromatic hydrocarbons (PAHs) which undergo charge separation reactions. In addition to collision-induced dissociation (CID), surface-induced dissociation\(^\text{24}\) was also performed. Collisions on both silicon and graphite surfaces showed that C_{60} does not dissociate appreciably at collision energies in the range of 200–300 eV. A number of studies have confirmed this unusual stability and has been attributed to the ‘resilience’ of the molecule. Similar properties have been predicted for its hydrides also\(^\text{25}\). C_{60} collision also leads to delayed ionization and thermionic emission\(^\text{26}\).

Surface collision experiments have been reported on higher fullerenes and metallofullerenes as well\(^\text{27}\). Mass spectrometry has also been used to study thermodynamic properties of fullerenes\(^\text{28}\).

In addition to the fragmentation, endohedral complex formation is also observed when high energy collisions are performed\(^\text{29}\). Eight keV collision of helium with C_{60}^+ produced a number of C_{n+4}^+ mass peaks. When the collision gas was changed to ^{3}He, the peaks shifted by one
mass unit showing that the peak was due to the addition of helium atoms to C$_{60}$. Others did experiments in different types of hybrid tandem mass spectrometers and confirmed the results. Ion kinetic energy and CID measurements showed unambiguously that He$^+$@C$_{60}$ (the @ symbolism implies that the species prior to @ is within the cage of the fullerene after the symbol) is an endohedral complex. Similar measurements were repeated with C$_{60}^{2+}$ and C$_{60}^{3+}$. C$_{70}^+$ and C$_{84}^+$ were also shown to form endohedrals. Ne$^+$@C$_{60}$ and Ar$^+$@C$_{60}$ are hard to observe in conventional spectrometers due to large energy losses, but they have been seen in specially designed instruments (see also the section on endohedral complexes).

In addition to the work on pure C$_{60}$, mass spectrometry has been used extensively to characterize the derivatives of C$_{60}$ formed by reactions$^{30}$. The identification of Birch reduction products of C$_{60}$ was done with electron impact (EI) mass spectrometry. The products of C$_{70}$ were also studied by EI. Reaction products with fluorine showed mass peaks at C$_{60}$F$_{36}^+$ and C$_{70}$F$_{40}^+$. These products fragment by elimination of F, CF$_3$ and C$_2$F$_3$. Methylated C$_{60}$ showed products with 1 to 24 methyl groups. C$_{60}$ and C$_{70}$ were found to add to aromatic molecules such as benzene, toluene, xylene, anisole and bromobenzene$^{31}$. (See Box 2 for a discussion of the chemistry of fullerenes.)

The fullerene cage itself could include other elements such as boron$^{32}$ and nitrogen$^{33}$. Evaporation of boron nitride doped graphite disk produced boron doped fullerenes$^{32}$ such as C$_{60}$nB$_n^+$ with n = 0 to 6. Photodissociation showed that these species are resistant to fragmentation, but reactions with ammonia showed the acidic behaviour of boron atoms. Species such as C$_{60}$nB$_n$(NH$_3$)$_n^+$ were observed showing that boron has been incorporated into the cage. Substituted fullerenes such as C$_{60}$NH are now prepared by synthetic chemistry$^{34}$.

Photoionization time of flight mass spectrometry has been used to show that clusters of C$_{60}$ are indeed formed during evaporation$^{35}$. Intensity anomalies in the mass spectrum have been detected corresponding to (C$_{60}$)$_n^+$ where n = 13, 19, 23, 35, 39, 43, 46 and 55. The numbers suggest that the closed shell clusters $n = 13$ and 55 are probably icosahedra. The magic numbers are similar to the clusters of Xe and Ar. In Figure 6 we show the structure of the icosahedral cluster, (C$_{60}$)$_{13}$.

Fullerenes undergo coalescence reactions in the gas phase. In laser evaporation of fullerene films, it was found that the mass spectra show peaks at very high masses above m/z 720 with enhanced intensities in the range of (C$_{60}$)$_n^+$ (Figure 7)$^{36}$. This proposes the fusion of C$_{60}$ cages to form larger cage structures. The identity of the products was also studied by surface-induced dissociation, which showed that the clusters are hard to dissociate and no parent fullerene is formed. This excludes the interpretation that the peaks could be due to di-fullerene-like structures. The reaction is supposed to be taking place in the excited dense plasma. Similar coalescence reactions have been reported by others also.
Box 2. Chemistry of fullerenes in the condensed phase

Originally it was thought that $C_{60}$ is an aromatic molecule because there are about 12,500 possible resonance structures. However, it should be remembered that in systems where pentagons are near hexagons, the system avoids double bonds in pentagons. The presence of double bonds in pentagons reduces the bond distances, increasing the strain. For $C_{60}$ there is only one structure which avoids double bonds in pentagons. This means that the delocalization of electrons is poor and $C_{60}$ is poorly aromatic\textsuperscript{31}. This 'poorly aromatic' classification immediately suggests certain type of chemistry. $C_{60}$ can be visualized in terms of coronene subunits with two distinct chemical bonds. The 60 6–6 bonds (between hexagons) with a bond length of ca. 1.38 Å have more double bond character than the 60 6–5 bonds (between pentagons and hexagons) of bond length ca. 1.45 Å; which are more like single bonds. This means that the pentagonal rings are extremely strained and insertion of a double bond in the 6–5 ring can bring in instability to the tune of 8.5 kcal/mol (ref. 126). However, describing its chemistry in terms of substructures such as radialene and paracyclohexyl (see Figure 1) does not reflect the chemical reality fully since these substructures are planar while fullerenes are spherical. Fullerenes are strained and continuous and describing their chemistry in terms of a strained weakly aromatic molecule may be more appropriate\textsuperscript{37}.

Since fullerenes have only carbon atoms, substitution reactions cannot be done with them. However, such reaction could be done on its derivatives. The cages consist of sp\textsuperscript{2} hybridized carbon atoms which have π inductive effect. Therefore, fullerenes are strongly electron attracting and they react readily with nucleophiles and the reactions are similar to those of poorly-conjugated alkenes. The important problem is the number of addition products each reagent is going to bring about. A given product can also have a large number of structural isomers. Added to this, they may have very little solubility in organic solvents. Many of them do not have high stability due to the strain caused by the addition and therefore they may revert to parent fullerene under mass spectrometric examination. Only a few of them crystallize easily so that single crystal examination is possible. Added to this, the study has to be performed with very small quantity of material, often milligrams, although the situation has substantially improved in recent years. Sometimes, the purification procedures leave only tiny quantities of pure compound at the end. In many a case, purification of isomers is very difficult which makes complete understanding of the chemistry extremely time consuming, often impossible. Therefore, a large number of reactions are still not fully studied. However, there are certain investigations which stand out and have resulted in unique products. Because of its comparatively easy availability and due to its unique symmetry, $C_{60}$ has been subjected to more detailed examinations.

Early electrochemical studies suggested that fullerene $C_{60}$ undergoes six reversible reductions\textsuperscript{128} corresponding to the complete filling of the $t_{1u}$ LUMO. The early $C_{60}$ chemistry revolved around this high electron affinity of the cage. Adducts of $C_{60}$ with radicals, nucleophiles, carbenes and dienophiles have been reported. Functionalization leading to π–π complexes of transition metals\textsuperscript{129} was the early organometallic chemistry reported. Alkylation of $C_{60}$ leading to methanofullerenes\textsuperscript{130} is being intensely pursued by the groups of Wudl, Rubin and Diederich. A detailed account of this can be found in a recent book by Hirsch\textsuperscript{5}. Those reactions have been shown to result in fullerene polymers\textsuperscript{131}, fullerene dendrimers\textsuperscript{132} (see Figure 5), fullerene-based HIV protease inhibitors\textsuperscript{133}, fullerene nucleotide conjugates\textsuperscript{134} and a number of other potentially useful materials. The electrochemical and photophysical characteristics of fullerene adducts can be technologically interesting. Although the chemistry of $C_{60}$ is intensely investigated, that of higher fullerenes is beginning to attract attention. Because of the presence of large number of non-equivalent bonds, the product distribution is more complex. Nanotubes of carbon are also subjected to solution phase chemistry in a number of laboratories\textsuperscript{135}.

Another type of reaction which has not been observed before has been the addition of $C_{60}$ and $C_{70}$ in the gas phase\textsuperscript{37}. In this study, a $C_{60}$ film was bombarded by high energy ions. The mass spectrum of the produced ions shows peaks at $C_{60}$, $C_{60}+$, $C_{60}+$, etc. all the way up to $C_{106}$, the mass limit of the instrument as shown in Figure 7. This suggests that the $C_{n}$ fragments add back to $C_{60}$ in the region called 'selvedge', the region immediately above the condensed phase where ion/molecule reactions occur. In fact such addition reactions are shown to occur without any activation barrier\textsuperscript{35}.

Endohedral chemistry of fullerenes

The cavity in the 7 Å diameter buckminsterfullerene molecule has intrigued chemists ever since the discovery
ions and noble gases were shown to result in noble gas encapsulated fullerenes. For a substantial period of time, characteristic mass spectral fragmentation pattern was the only experimental evidence for the existence of endohedral fullerenes. The fact that He could be put into the cage prompted Saunders to probe the chemistry of endohedrals through $^3$He NMR. Rg@C$_{60}$ (Rg = rare gas) molecules have been synthesized by a high temperature–high pressure method. Studies showed the high diamagnetic shielding of the inner C$_{60}$ surface indicating the existence of a high degree of aromaticity. The $^3$He endohedral chemistry is now being extended to the study of derivatives of C$_{60}$ (refs 43, 44) and isomers of higher fullerenes. Results show that there are at least eight C$_{78}$ isomers and nine C$_{84}$ isomers, much higher than originally suggested. La@C$_{82}$, La@C$_{80}$, La@C$_{78}$ and a number of Y, Sc and Mn endohedrals have been prepared and purified. The electrochemical, electronic and magnetic properties of these materials have been investigated. Gd@C$_{82}$ is paramagnetic down to 3 K (ref. 47). There are theoretical predictions on the various electronic properties of endohedrals but experimental confirmation is awaited. A recent development in the endohedral chemistry is the preparation of Li@C$_{60}$ by low energy ion-beam collision of Li$^+$ on a C$_{60}$ film.

**Orientational ordering**

Of the several properties of fullerenes, a widely investigated aspect is the orientational ordering. Generally molecules of a high point group symmetry crystallize with a certain degree of orientational disorder. Some lower fullerenes are highly spherical and are held together by weak van der Waals forces, the molecular orientations need not be ordered as in the case of an ordered crystal. This high asymmetry is evidenced by the fact that large thermal parameters are necessary to fit the observed diffraction patterns. This symmetry is the reason why C$_{60}$ had to be fixed with a handle by complexation to refine the atomic positions as was done by Hawkins.

In the pure form, because of its high symmetry and weak intermolecular interaction, C$_{60}$ rotates freely in the lattice. This may lead to interesting properties such as the unusual flow of liquids over C$_{60}$ film. This rotation can be frozen at low temperatures, resulting in an orientational ordering. Upon reaction or by co-crystallization, which inhibits free rotation of C$_{60}$ molecules, the atomic positions have been studied. At room temperature, C$_{60}$ gives a sharp NMR signal at 143 ppm and the signal broadens at low temperatures as a result of chemical shift anisotropy. This is due to the dynamic nature of the disorder, the orientational correlation times are of the order of 16 picoseconds. The orientationally
disordered fcc phase undergoes a transition to a sc phase at 248 K (ref. 51). In Figure 8, a differential scanning calorimetry trace of the transition is shown. In the sc phase, the rotation exists only along preferred axis. NMR studies have shown that below the ordering temperature the molecules jump between preferred orientations over a barrier of 3000 K (ref. 50). Phase transitions can be modelled which show that simple L-J potentials reproduce experimental behaviour. Charge-transfer effects are, however, important. Neutron diffraction studies indeed provide a strong support to this suggestion in which it is found that the electron-rich bonds of one molecule are located close to the electron poor pentagon rings of the adjacent molecule.

Orientational ordering results can be seen in IR and Raman spectroscopies also. A glassy phase has been observed around 80 K when molecular rotations are completely frozen. It may be mentioned that many of the derivatives of C₆₀ are also spherical and phase transitions of this type may be observed in them. Recently we have observed such a transition in C₆₀Br₃₄.

C₇₀ undergoes two phase transitions at 337 and 276 K and these transitions have been studied by IR and Raman spectroscopies. Diffraction studies suggest a monoclinic structure for the lowest temperature phase and rhombohedral or hexagonal structure for the in-between phase. Complete orientational freezing happens only at 130 K. Upon phase transition, the intramolecular phonons undergo hardening, a general feature observed for both C₆₀ and C₇₀. Resistivity measurements have proved that there are two phase transitions in C₆₀ and three in C₇₀ (ref. 59).

**Pressure effects**

Both C₆₀ and C₇₀ are soft solids and their compressibilities are comparable to the c-axis compressibility of graphite. Upon application of pressure, the orientational ordering temperature increases at a rate of 10 K/kbar (ref. 60). Around 20 GPa, C₆₀ undergoes a transition to a lower symmetry structure. Above 22 GPa the material undergoes amorphization and the phase shows evidence for sp³ hybridized carbon. In C₇₀ amorphization happens around 12 GPa and only sp³ hybridized carbon is seen. This suggests that while polymerization via Diels–Alder addition might be happening in C₆₀, no such reaction occurs in C₇₀. Polymerization upon light irradiation has been observed in C₆₀ (ref. 63). Under extremely high pressures, it is possible to convert C₆₀ to diamond at low temperatures. Such a conversion is seen in C₇₀ also.

At fairly low pressures below the amorphization pressure, the photoluminescence band originally at 1.6 eV undergoes a redshift. At a pressure of 3.2 GPa the band merges with the background, corresponding to the collapse of the photoluminescent gap. This arises due to the broadening of the HOMO and LUMO which is a result of shortening of the inter-molecular distance and concomitant increase in the interball hopping integral. This study has implication to the low temperature electrical properties found in doped fullerenes.

**Conductivity and superconductivity in doped fullerenes**

Doping with potassium, corresponding to the stoichiometry K₃C₆₀, produces a superconductor with a transition temperature of 19.8 K (refs 66, 67) (Figure 9). The K₃C₆₀ phase
was earlier found to be metallic. It is interesting to note that doping graphite with potassium also results in superconductivity, but at extremely low temperatures. However, doping of Na and Li does not result in superconductivity, but other alkali metals do produce superconductors with higher transition temperature ($T_c$). Mixtures of metals also show the same phenomenon. Because the $t_{2u}$ LUMO is triply degenerate, six electrons can be pumped into $C_{60}$. Six more can be placed in the $t_{1u}$ LUMO. These electrons can be easily transferred from metal atoms placed in the tetrahedral and octahedral voids of fcc $C_{60}$. The highest $T_c$ organic superconductor, Rb$_2$CsC$_{60}$ has a $T_c$ of 31 K (ref. 69). A$_2$B$_{20}$ (bcc) and A$_2$C$_{60}$ (bcc) have transition temperatures greater than that of $C_{60}$. Electron spectroscopy shows that continuous filling of the LUMO happens upon doping but on prolonged exposure, the LUMO band is shifted below $E_F$ making it an insulator. Upon exposure to transition metals, the $d$ states grow near $E_F$ and incomplete metal to $C_{60}$ charge transfer is observed. Studies show that $T_c$ is a function of interband separation. Thus, intramolecular phonons are responsible for the superconducting ground states in these materials. Superconductivity in A$_2$C$_{60}$ has been treated as a special case of BCS theory with intermediate electron-phonon coupling. Ca$_2$C$_{60}$ (ref. 74), Ba$_2$C$_{60}$ (ref. 75) and Sm$_2$C$_{60}$ (ref. 76) are superconducting. Superconductivity in fullerences has not been reported, probably due to lower symmetry.

Ferromagnetism in $C_{60}$ TDAE

Another important property which arises as a result of charge-transfer is ferromagnetism. Organic ferromagnetism is a rare phenomenon and is proved conclusively only in a few systems. So far there is only one donor which is shown to produce ferromagnetism as a result of complexation with $C_{60}$, which is TDAE, tetrakis(dimethylamino)ethene. The $T_c$ observed is 16.1 K, which is the highest $T_c$ found for an organic material so far. The material belongs to the monolonic system with short $C_{60}$ contact along $a$ axis. The quasi one-dimensional behaviour has been suggested by susceptibility measurements also. Single electron transfer has been confirmed by EPR and Raman studies. Magnetic and electrical transport properties of $C_{60}$ TDAE have been reported on single crystals also. A number of organic donors have been investigated for potential organic magnetism. Though all of them show pronounced magnetic correlation, no ferromagnetism has been reported. In $C_{60}$ TDAE, spontaneous magnetization has been verified by zero-field muon spin relaxation technique as well.

Optical properties

$C_{60}$ trapped in molecular sieves gives intense red light. Light transmitting properties of $C_{60}$ embedded silica films have been investigated. $C_{60}$ is found to be an interesting material for nonlinear optics, especially for third harmonic generation. Optical susceptibility of $C_{60}$ film is interpreted in terms of the totally symmetric ground state along with two excited states; a one-photon state and a two-photon state. Photoconductivity and photoinduced electron transfer, optical switching properties and second harmonic generation are also thoroughly investigated. Several recent conferences have devoted exclusive sessions on the photophysics of fullerenes.

Two unusual properties

$C_{60}$ shows anomalously solubility behaviour. Normal solutes show a linear temperature dependence of solubility. In most cases, the solubility increases with increasing temperature. Inorganic systems unusual phenomena are seen due to solute-solvent interactions. Studies of solubility of $C_{60}$ studied in a number of solvents indicate that there is a solubility maximum at near-room temperature (280 K), dissolution is endothermic below room temperature and exothermic above. The results have been interpreted as due to a phase change in solid $C_{60}$ modified by wetting due to solvent. Solubility maximum in organic materials is unprecedented.

Ordinary materials have a critical point above which the distinction between liquid and solid disappears. The liquid is not seen below the triple point where solid and liquid coexist. $C_{60}$ is one substance in which no liquid phase exists according to theoretical investigations of the phase diagram, although the question is still not resolved. If at all such a liquid phase exists, it will be only at high temperatures above 1800 K where the molecules may not be stable.

Carbon nanotubes and onions

Fullerenes need not be found in spherical shape. Upon DC evaporation of carbon, the material deposited on the cathode was found to have tube-like structures of several nanometer length with closed tips such as the one shown in Figure 10. Not only five and six but also seven-membered rings are found in these tubes. There can be single-walled tubes, but most are multi-walled. These tubes are less susceptible to combustion; therefore, heating in oxygen is a method of cleaning them. The most essential feature of nanotube formation appears to be the presence of high electric fields at the tip of the tubes. The presence of carbon-inert gas plasma make the growing tube end fluid-like. The mechanism is akin to the electrochemical growth processes. The growing tube end closes as a result of instabilities in the plasma. The tubes thus formed have been
characterized by X-ray diffraction\textsuperscript{95} and Raman\textsuperscript{96} spectroscopy.

The structure of nanotubes makes their electronic properties very interesting. Calculations show that these materials could be good electrical conductors\textsuperscript{97} and even superconductors (below 1 mK)\textsuperscript{98} and the diameter of these tubes can be varied to tune the electrical transport properties. Experimental studies show that the tubes are semiconducting and the behaviour is similar to graphite\textsuperscript{99}. Mechanically, the tubes do not have high aspect ratios, making them unsuitable for reinforcing purposes. However, experiments are underway to improve this parameter\textsuperscript{100}. A recent application of nanotubes is their use in STM as contact tips.

Tubes can be filled with metals upon opening the tips with oxygen\textsuperscript{101}. The probability of making nanoscale wires of metals has enthused many scientists. Lead has been put into the tubes by heating the tubes with lead oxide\textsuperscript{95}. Such materials may have interesting magnetic properties\textsuperscript{102}. Tube tips can also be opened by chemical methods such as boiling with HNO\textsubscript{3} and if boiled in the presence of metal salts, metals can be incorporated into the tubes.

Carbon onions are also formed along with tubes. These near-spherical large molecules are also found with single or multiple shells and can be filled with metal or metal-carbide particles\textsuperscript{103}. Nanoparticles of metals could be placed in these onions so that they are resistant to oxidation, at the same time physical properties such as magnetism are unaffected. It has been found that the electron beams of a TEM can be used to open the onion, stuff it with metal and empty it again\textsuperscript{104}. It is also possible to use the onion shell as pressure vessels so that the graphite inside can be converted to diamond upon electron beam exposure\textsuperscript{105}.

**Perspectives**

The science of fullerenes is still dominated by chemical physics aspects. A quick glance through the literature of the past two years shows that organic chemistry of fullerenes is still in its infancy. The challenges involved in the characterization of derivatives are understandable and complete understanding of a particular reaction requires the application of several tools simultaneously. Therefore, it is very clear that chemical physics and related areas will continue to dominate fullerene research. Of course in the near future, carbon tubules and onions will add more colour to the physics and chemistry of carbon. Materials science of fullerenes is one area which has reached a certain stage of maturity and Indian contributions are particularly noteworthy\textsuperscript{106}. Buckyball has brought delight to theorists and the excitement will continue. But it is a pity that in spite of the great many discoveries made, fullerenes have not made long inroads into other areas. C\textsubscript{60} and its brothers have collectively caught our imagination and in effect it has become the most intensely researched single molecule of 20th century. Probably it may indeed be its greatest legacy.

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