Crystal Structure of Fullerene C60 & C70 – A Theoretical Approach

Dr. Vaibhav Jain
Physics Department, DAV (PG) College, Bulandshahr, UP, India.

Theoretical study of fullerene C60 and C70 via Raman Spectra method were performed to investigate the Crystal *structure of fullerene C60 and C70. . Raman Spectroscopy is particularly well suited to detect small changes in structural morphology of carbon nano materials making it an indispensable tool for many material scientists working with carbon nanostructures. Structure of fullerene C60 lead to interesting application possibilities. And its derivatives such as buckyball clusters, nanotubes, megatubes, polymers, nano onions and fullerene rings have made fullerenes as an active field of research.*

Keywords: fullerene, buckminsterfullerene.

1. INTRODUCTION

While the possibility of a stable closed-cage molecular structure for carbon was first suggested in 1970 [1], the existence of fullerenes was not verified experimentally until 15 years later [2]. Laser ablation of a graphite target was used to create carbon clusters. Mass spectra of the resultant vapor revealed the synthesis of molecules in two main groups – rings consisting of 10- 30 atoms and larger molecules with predominantly 60 and 70 member atoms [3]. Researchers soon theorized that these high-mass molecules possessed a closed-cage configuration. The name “Fullerene” was coined after R. Buckminster Fuller, an architect renowned for his construction of geodesic domes resembling the structure of these molecules. (Figure 1). Raman spectroscopy is particularly well suited to molecular morphology characterization of carbon materials. Every band in the Raman spectrum corresponds directly to a specific vibrational frequency of a bond within the molecule. The vibrational frequency and hence the position of the Raman band is very sensitive to the orientation of the bands and weight of the atoms at either end of the bond.

2. Raman Spectra

Raman spectrum of diamond is compared to the Raman spectra of crystalline silicon and germanium. These spectra show us several things. First, note that in the case of diamond, where the material consists of highly uniform C-C bonds in a tetrahedral crystal structure, the Raman spectrum is very simple.

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Fig. 1: Buckminsterfullerene.

It consists of only a single band because all of the bonds in the crystal are of the same orientation and strength resulting in a single vibrational frequency. We also see that the spectrum of diamond is easily distinguished from the spectra of silicon and germanium by the frequency (cm^{-1} position)

of the band even though they share the same tetrahedral crystal configuration. The heavier atoms of silicon and germanium slow the vibrational frequency and shift the corresponding Raman band to lower frequency as well. Similarly when we compare the Raman spectra of two carbon allotropes – diamond and graphite – again we can easily distinguish the two materials by their Raman spectrum even though both are composed entirely of C-C bonds. The graphite spectrum has several bands in the spectrum and the main band has shifted from 1332 cm-1 in diamond to 1582 cm-1 in graphite. The reason for this is that graphite is composed of sp2 bonded carbon in planar sheets in which the bond energy of the sp2 bonds is higher than the sp3 bonds of diamond. The higher energy of the sp2 bonds in graphite pushes the vibrational frequency of the bonds and hence the frequency of the band in the Raman spectrum to higher frequency. The 1582 cm-1 band of graphite is known as the G band. The presence of additional bands in the graphite spectrum indicate that there are some carbon bonds with different bond energies in the graphite sample and this is in fact the case, as graphite is not quite as uniform in structure as diamond.

The vibrational Raman spectroscopy of fullerene C70 has attracted much attention since C70 was obtained in 1990.[4] Samples of mixtures of C60 and C70 were first used in the measurement, which led to tentative assignments of the strong peaks.[5] Dennis et al.[6] then reported the Fourier transform Raman spectrum of C70 from pure samples. Subsequent Raman scattering measurements were carried out on C70 samples in the form of thin films,[7] crystals,[8] and solutions.[9-10].

Fullerenes: Fullerenes are essentially hollow carbon shells of various sizes.The most well known of these is a 60-carbon unit called Buckminster fullerene or C60. There are many other fullerenes, from a few to many hundreds of carbon atoms. compares the

Raman spectra of C60 and C70. The main feature in the C60 spectrum is a relatively sharp line at around 1462 cm-1, known as the pentagonal pinch mode. This tells us several things. Firstly, it tells us that C60 is composed of sp2 bonded carbon. The sharpness of the band also tells us that the bonds are for the most part very uniform in nature. In fact, the carbon atoms in C60 are equivalent and indistinguishable. In contrast, the spectrum of C70 is littered with numerous bands. This is due to a reduction in molecular symmetry which results in more Raman bands being active. Additionally Raman can also be very sensitive to doping and stress due to temperature or pressure.

Raman is a very powerful and valuable technique that can be of great benefit to characterization of carbon nanomaterials. Raman is particularly well suited to detect small changes in structural morphology of carbon nanomaterials making it an indispensable tool for many material scientists working with carbon nanostructures.

3. RESULTS AND DISCUSSION

Buckminsterfullerene is the smallest fullerene molecule in which no two pentagons share an edge (which can be destabilizing, as in pentalene). The Structure of a Buckminsterfullerene C60 is a truncated (T = 3) icosahedron, which resembles a soccer ball of the type made of twenty hexagons and twelve pentagons, with a carbon atom at the vertices of each polygon and a bond along each polygon edge. The van der Waals diameter of a C60 molecule is about 1.1 nanometers (nm) [11].The nucleus to nucleus diameter of a C60 molecule is about 0.71 nm. The C60 molecule has two bond lengths. The 6:6 ring bonds (between two hexagons) can be considered "double bonds" and are shorter than the 6:5 bonds (between a hexagon and a pentagon). Its average bond length is 1.4 angstroms. Each carbon atom in the structure is bonded covalently with 3 others Carbon Atoms have 6 Electrons, meaning their electronics structure is (2, 4). To become stable, the carbon atom ne other atoms will only make 7 Electrons in its outer shell. This means that one unbounded electrons on every carbon atom is free to float around all of the compound’s atoms.

Electronics carry charge, so this free electron movement means that the Buckminsterfullerene can conduct electricity very well. This, because of its size, makes it very useful in nanotechnology.

The structure of a fullerene is a trivalent convex polyhedron with pentagonal and hexagonal faces. In graph theory, the term fullerene refers to any 3-regular, planar graph with all faces of size 5 or 6 (including the external face). It follows from Euler's polyhedron formula, $V - E + F = 2$, (where V, E, F are the numbers of vertices, edges, and faces), that there are exactly 12 pentagons in a fullerene and $V/2 - 10$ hexagons.ed 8 Electrons in its outer shell and covalently bonding with 3 other atoms will only make 7 Electrons in its outer shell. This means that one unbounded electrons on every carbon atom is free to float around all of the compound’s atoms. Electronics carry charge, so this free electron movement means that the Buckminsterfullerene can conduct electricity very well. This, because of its size, makes it The proposed structure for C60, a"truncated icosahedron", is derived from an icosahedrons by truncating or "snipping off" each of the twelve vertices . Hence, eachvertex is replaced by a five-membered ring - a pentagon. This snipping process also converts each of the twenty former triangular faces into six-membered rings – hexagons, Icosahedron (left) and "truncated icosahedron" (right).very useful in nanotechnology. The structure of a fullerene is a trivalent convex polyhedron with pentagonal and hexagonal faces. In graph theory, the term fullerene refers to any 3-regular, planar graph with all faces of size 5 or 6 (including the external face). It follows from Eulers polyhedron formula, $V - E + F = 2$, (where V, E, F are the numbers of vertices, edges, and faces) Figure 5(a**)** Various fullerene 2 D structure. The proposed structure for C60, a"truncated icosahedron", is derived from an icosahedrons by truncating or "snipping off" each of the twelve vertices (Figure 5). Hence, each vertex is replaced by a five-membered ring - a pentagon. This snipping process also converts each of the twenty former triangular faces into six-membered rings - hexagons., that there are exactly 12 pentagons in a fullerene and V/2 – 10 hexagons.

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The smallest fullerene is the dodecahedral C20. There are no fullerenes with 22 vertices [12]. The number of fullerenes C2n grows with increasing n = 12, 13, 14..., roughly in proportion to n9. For instance, there are 1812 non-isomorphic fullerenes C60. Note that only one form of C60, the buckminsterfullerene alias truncated icosahedrons, has no pair of adjacent pentagons (the smallest such fullerene). To further illustrate the growth, there are 214,127,713 non-isomorphic fullerenes C200, 15,655,672 of which have no adjacent pentagons.

4. PROPERTIES

For the past decade, the chemical and physical properties of fullerenes have been a hot topic in the field of research and development, and are likely to continue to be for a long time.

4.1. Physical appearance

The purified fullerenes have very attractive colours. Thin films of C60 are mustard coloured (dark brown in bulk) and solutions in aromatic hydrocarbons are a beautiful magenta. Thin films of C70 are reddish brown (grayish-black in bulk) and solutions are port-wine red. C76, C78 and C84 are yellow in colour.

4.2. Chemical reactivity

According to the researchers fullerenes are considered to be the stable molecules but not fully unreactive. In certain circumstances fullerene become reactive. The reactive characteristics of fullerene are electrophilic at double bonding, which reduces angle stress by changing hybridized carbons into sp3 hybridized ones. Due to the change in hybridized orbits, the bond angles tend to decrease from about 120° in orbitals of sp2 carbon atoms. This decrease in bond angles permits the bonds to bend lesser on closing the tube making fullerene molecule more stable and the characteristic reaction of fullerenes is electrophilic addition at 6, 6-double bonds, which reduces angle strain by changing sp2-hybridized carbons into sp3- hybridized ones. Other atoms can be trapped inside fullerenes to form inclusion compounds known as endohedral fullerenes. Fullerenes undergo Hydrogenation, Addition, Functionalization , Oxidation and Reduction [13].

4.3. Solubility

Fullerenes are sparingly soluble in many solvents. Common solvents for the fullerenes include aromatics such as toluene and carbon disulfide. Solutions of pure Buckminsterfullerene have a deep purple colour or voilet colour. Colour solutions of C70 are a reddish brown. The higher fullerenes from C76 to C84 have different colour according to the portion mixed with solvents. Fullerenes are the only present allotrope of carbon that has the property to get dissolved in common solvents at normal room temperature. But in some cases fullerene structures remain undissolved [14]. Such as at their excite state these carbon allotropes are not soluble.

4.4. Aromaticity

Aromaticity is the reactivity of the certain material or molecule with other in the different tempe siuations. According to the Huckel's rule the aromaticity of fullerene is three dimentional. This property can be improved and managed according to the situation with the help of quantum chemical modelling which can empower the bonding. As a result, C60 in water tends to pick up two more electrons and become an anion.

4.5. Safety and toxicity

When focusing the toxic effects of the fullerene, it should be kept in mind that fullerene is not toxic in all forms. The physical bond of fullerene C60 is safe and non toxic but the derivatives of fullerenes could be harmful to the health [15]. Other fullerenes with covalently bonded chemical groups such as fullerene complexes, host-guest complexes and cyclodextrin are highly toxic [16]. Aggregation of nano particles of C60, and C70 crystallites in much larger form encourages the toxicity.rature. Fullerene also has aromaticity in different situations. A spherical fullerene has pi bonding electrons which are free to localize or delocalizein different chemical.

4.6. Superconductivity

After the synthesis of macroscopic amounts of fullerenes their physical properties could be investigated. Haddon et al. [16] found that intercalation of alkali-metal atoms in solid C60 leads to metallic behaviour. In 1991, it was revealed that potassium-doped C60 becomes superconducting at 18 K [18]. This was the highest transition temperature for a molecular superconductor. Since then, superconductivity has been reported in fullerene doped with various other alkali metals. It has been shown that the superconducting transition temperature in alkaline-metal-doped fullerene increases with the unit-cell volume V. As caesium forms the largest alkali ion, caesium-doped fullerene is an important material in this family. Recently, superconductivity at 38 K has been reported in bulk Cs3C60, but only under applied pressure. The highest superconducting transition temperature of 33 K at ambient pressure is reported for Cs2RbC60. The increase of transition temperature with the unit-cell volume had been believed to be evidence for the BCS mechanism of C60 solid superconductivity, because inter C60 separation can be related to an increase in the density of states on the Fermi level. Therefore, there have been many efforts to increase the interfullerene separation, in particular, intercalating neutral molecules into the A3C60 lattice to increase the interfullerene spacing while the valence of C60 is kept unchanged. However, this ammoniation technique has revealed a new aspect of fullerene intercalation compounds.

The C60 molecules compose a solid of weakly bound molecules. The fullerites are therefore molecular solids, in which the molecular properties still survive. A fully developed theory of C60 solids superconductivity is still lacking, but it has been widely accepted that strong electronic correlations and the Jahn-Teller electron-phonon coupling produce local electron-pairings that show a high transition temperature close to the insulator-metal transition.

5. Applications

Because of the unique structure and properties, fullerenes draw lots of attention from Physicists, Chemists and Engineers who are trying to find some potential applications of these new carbon structures. Some potential applications for fullerenes include:

5.1. Lubricant additives

Physically, buckyballs are extremely strong molecules, able to resist great pressure-they bounce back to the original shape after being subjected to over 3000 atmospheres. This gives buckyballs, graphite like potential as a lubricant.

5.2. Optical devices

Fullerenes have interesting electrical properties, which have led to suggestions for use in number of electronics related areas. The same properties offer potential use in photo detectors for X-rays.

5.3. Data storage devices

Fullerenes have been inserted into nanotube, the result sometime referred to as ‘peapods’, the properties can be modified by moving the location of the enclosed fullerens and research has even suggested using this to create memory devices.

5.4. Fuel cells

Another use of electrical property of fullerenes is in fuel cells exploiting their ability to help proton move around and Proton exchange membranes for fuel cells, work as portable power. Hydrogen storage as almost every carbon atom in C60 can absorb a hydrogen atom without disrupting the buckyball structure, making it more effective than metal hydrides. This could lead to applications in fuel cells.

5.5. Liquid crystal display

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6. CONCLUSIONS

Fullerenes belong to a fundamentally new class of molecules and also constitute a new allotrope of carbon. The discovery of this new family of non-planar carbon compounds has generated immense interest within the scientific field with the thousand of paper published about fullerenes and fullerene based materials. Because of its discrete molecular nature, it is the only pure form of carbon. Unlike diamond and carbon, this new allotrope is made up of hollow carbon cages. The number of carbon atoms in each fullerene cage can vary and due to this reason numerous new structures can be imagined. Because of their unique chemistry, fullerenes are extensively used in the fields of materials science, electronics, and nanotechnology etc. Thus, we conclude that the structure of fullerene C60 lead to interesting application possibilities. And its derivatives such as buckyball clusters, nanotubes, megatubes, polymers, nano onions and fullerene rings have made fullerenes as an active field of research.

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