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Crystal Structure of Fullerene C_{60} & C_{70} – A Theoretical Approach

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Crystal structure of fullerene C_{60} and C_{70} with the help of Raman Spectra were studied by many scientists earlier. Particularly Raman Spectroscopy is well suited to detect small changes in structural morphology of carbon nano materials making it an indispensable tool for many materials with carbon nanostructures. Structure of fullerene C_{60} and C_{70} lead to interesting application possibilities. Derivatives of C_{60} and C_{70}, such as buckyball clusters, nanotubes, megatubes, polymers, nano onions and fullerene rings have many interesting applications which made fullerenes as an active field of research.

Keywords: Fullerene, Raman Spectra, Buckminsterfullerene.

1. INTRODUCTION

The possibility of a stable closed-cage molecular structure for carbon was first suggested in 1970 [1]. It was in the early 1980's, when the astronomers observed a distinct narrow hump at 2175 Å wavelength in the extinction spectrum of light i.e., sum of scattering and absorption losses, of the interstellar medium, which indicated the presence of cluster of pure carbon or molecular form of carbon in the space. The calculations of the extinction spectrum from spherical cage-like graphite clusters of diameter ~10 Å generated such a hump. Efforts were made to produce such carbon clusters in laboratories and in 1985, a joint Sussex/Rice Universities research team including H.W. Kroto, R.F. Curl and R.E. Smalley [2], who were awarded Nobel Prize in 1996 for their discovery of 'fullerene' i.e. even-numbered carbon clusters greater than 30 carbon atoms. These clusters can be produced by focusing a powerful laser beam on a graphite sample in a quenching atmosphere of helium gas [3].

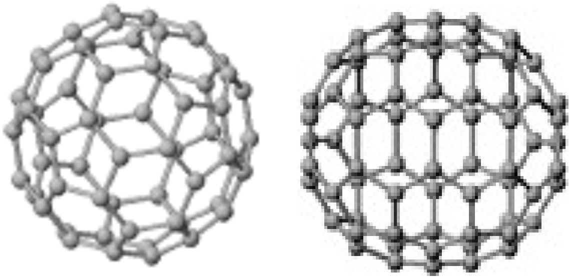

Fig. 1: Buckminsterfullerene (C_{60}) and C_{70}.

It has a structure similar to the distinctly stable geodesic structure suggested by the

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famous American architect Buckminster Fuller. C_{60} is, therefore, called Buckminsterfullerene or Buckyball. Its diameter is ~7.1 Å and all the carbon atoms on the 60 vertices are identical being located at the junctions of two hexagons and a pentagon as shown in Figure 1.

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. Hence Raman spectroscopy is well suited to molecular morphology characterization of carbon materials.

2. RAMAN SPECTRA OF C_{60} AND C_{70}

The vibrational Raman spectroscopy of fullerene C_{70} has attracted much attention since C_{70} was obtained in 1990 [4]. Raman spectrum and IR spectra of thin film samples of C_{60} give a complete set of Raman and infrared active fundamental frequencies for this molecule. A comparison of this set with the calculated spectrum for buckminsterfullerene shows satisfactory agreement [5].

Samples of mixtures of C_{60} and C_{70} were first used in the measurement, which led to tentative assignments of the strong peaks [5]. Dennis *et. al.* [6] reported that the Fourier transform Raman spectrum of C_{70} gives 27 bands out of the total of 53 that were theoretically predicted. These data will permit refinement of calculations of vibrational lines appropriate to closed-cage carbon clusters.

Subsequent Raman measurements were carried out on C_{70} samples in the form of crystals [7] shows that changing the crystalline environment of C_{60} has little effect upon the vibrational frequencies of the intramolecular vibrations but has some effect on relative intensities of peaks. The Raman polarization measurement of solutions of C_{60} allows an evaluation of the fundamental vibrations of the C_{60} molecule and for C_{70} the most extended set of Raman frequencies was found [9].

High-resolution FT-Raman spectra including solution spectra with polarization measurements, as well as IR spectra of C_{60} and C_{70} samples a correlation, in the sense of a genetic relationship, between C_{60} and C_{70} vibrations is developed which showed that all cluster vibrations cannot be modeled uniformly [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 C_{60}. There are many other fullerenes, from a few to many hundreds of carbon atoms. The main feature in the C_{60} Raman 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 C_{60} is composed of sp^2 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 C_{60} are equivalent and indistinguishable. In contrast, the Raman spectrum of C_{70} is littered with numerous bands. This is due to a reduction in molecular symmetry which results in more Raman bands being active. Additionally Raman spectra can also be very sensitive to doping and stress due to temperature or pressure.

Raman spectra is a very powerful and valuable technique that can be of great benefit to characterization of carbon nanomaterials. Raman spectra 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 C_{60} 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 [4]. The van der Waals diameter of a C_{60} molecule is about 1.1 nanometers (nm). The nucleus to nucleus diameter of a C_{60} molecule is about 0.71 nm. The C_{60} 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. The electronic structure of carbon atom is (2, 4). This means that one unbounded electrons on every carbon atom is free to float around all of the compound's atoms. Electrons 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 [11].

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 [12]. The proposed structure for C_{60}, a" truncated icosahedron", is derived from an icosahedrons by truncating or "snipping off" each of the twelve vertices. 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, Icosahedron (left) and "truncated icosahedron" (right). The smallest fullerene is the dodecahedral C_{20}.

One can produce pure crystals of C_{60}, which are large enough to be studied for their various properties. Such crystals are christened as 'fullerites'. Fullerite has melting point ~280 degree which is more than that of graphite and diamond .Under shock compression, C60 can be transformed into graphite layer.

Fullerite, exhibits quite different dynamics and physical properties. When doped with alkali metal like K, Rb, Cs becomes superconductor with high superconducting transition temperature, T_c, lying in between 19K to 33K depending upon the dopant. Such doped fullerites are referred to as fullerites and have the composition A_3C_{60}, where A is an alkali metal.

Olson *et. al.* [13] have reported the results of their measurements on their specific heat of polycrystalline C_{60} fullerite in the temperature range 0.2-300 K.

The temperature variation of the observed specific heat is in the range 0.2-300K is quite different from what has been observed in two other allotropes of carbon viz. diamond and graphite, particularly for temperatures less than ~100 K.

The dynamics of fullerite is quite complicated. The contributions to the specific heat from various kinds of dynamical modes like glassy modes are present giving rise to T dependent specific heat, graphite like modes indicated by T^3 dependence at low temperatures and graphite-like specific heat variation for >80 K. The contributions of anisotropic planer modes [14,15] is present throughout, right from 0.2K to 300K . Beyond this contribution there are mounted tunneling modes which contribute significantly at very low temperature $T<1K$. Librational and orientaional diffusive modes contribute significantly in the temperature range $2<T<80K$. Optical modes contribute for temperature $T>80$ K.

4. PROPERTIES

The fullerene structure is unique in that the molecule is borderless, uncharged, has no boundaries, no dangling bonds, and no unpaired electrons. These characteristics distinguish fullerene from other crystal structures, such as graphite or diamond, which have edges with dangling bonds and electrical charges. Fullerene is chemically reactive and can be added to polymer structures to form new copolymers with specific physical and mechanical properties.

4.1. Physical appearance

Fullerens are dark needle-like crystals at normal temperature. The purified fullerenes have very attractive colours. Thin films of C_{60} are mustard coloured (dark brown in bulk) and solutions in aromatic hydrocarbons are a beautiful magenta. Thin films of C_{70} are reddish brown (grayish-black in bulk) and solutions are port-wine red. C_{76}, C_{78} and C_{84} 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 sp^3 hybridized ones. Due to the change in hybridized orbits, the bond angles tend to decrease from about 120° in orbitals of sp^2 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 sp^2-hybridized carbons into sp^3- 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.

4.3. Solubility

Fullerenes are not soluble in water. 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 C_{70} are a reddish brown. The higher fullerenes from C_{76} to C_{84} 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 [16]. Such as at their excite state these carbon allotropes are not soluble.

4.4. Aromaticity

A spherical fullerene of n carbon atoms has n pi-bonding electrons, free to delocalize. These should try to delocalize over the whole molecule. The quantum mechanics of such an arrangement should be like only one shell of the well-known quantum mechanical structure of a single atom, with a stable filled shell for n = 2, 8, 18, 32, 50, 72, 98, 128, etc. (i.e., twice a perfect square number), but this series does not include 60. This $2(N + 1)^2$ rule (with N integer) for spherical aromaticity is the three-dimensional analogue of Hückel's rule. The 10+ cation would satisfy this rule, and should be aromatic. This has been shown to be the case using quantum chemical modelling, which showed the existence of strong diamagnetic sphere currents in the cation [17]. As a result, C_{60} in water tends to pick up two more electrons and become an anion. The nC_{60} described below may be the result of C_{60} trying to form a loose metallic bond.

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 C_{60} is safe and nontoxic but the derivatives of fullerenes could be harmful to the health. Other fullerenes with covalently bonded chemical groups such as fullerene complexes, host-guest complexes and cyclodextrin are highly toxic. Aggregation of nano particles of C_{60}, and C_{70} crystallites in much larger form encourages the toxicity nature [18].

4.6. Superconductivity

After the synthesis of macroscopic amounts of fullerenes their physical properties could be investigated. Haddon *et. al.* [19] 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. 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 cesium forms the largest alkali ion, cesium-doped fullerene is an important material in this family. Recently, superconductivity at 38 K has been reported in bulk Cs_3C_{60}, but only under applied pressure. The highest superconducting transition temperature of 33 K at ambient pressure is reported for Cs_2RbC_{60}. The increase of transition temperature with the unit-cell volume had been believed to be evidence for the BCS mechanism of C_{60} solid superconductivity, because inter C_{60} 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 A_3C_{60} lattice to increase the interfullerene spacing while the valence of C_{60} is kept unchanged.

A fully developed theory of C_{60} 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 have many physical, chemical and biological applications. Some potential applications are:

5.1. In Automotive Industry

Fullerenes could be used as electro catalysts. They could lower the pollution caused by the fossil fuels. They can enhance the properties of the coating agents. They can form composite and polymeric materials. They can be used as lubricants as 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 C_{60} 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.

6. CONCLUSIONS

Fullerenes belong to a fundamentally new class of molecules and also constitute a new allotrope of carbon. Its crystal structure determined by Raman spectroscopy gives valuable information which explains its physical and chemical properties. 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. Fullerenes are extensively used in the fields of materials science, electronics, and nanotechnology etc. The structure of fullerene C_{60} and its derivatives such as buckyball clusters, nanotubes, megatubes, polymers, nano onions and fullerene rings lead to interesting application possibilities.

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