Fullerene

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1 History

The idea of giant spherical carbon modification was first mentioned in a publication by Jones 1966. Unfortunately it didn’t get a lot of attention then. But this changed when Osawa published the first theoretical paper about fullerene in 1970. Therefore he has been inspired by the football of his son and made a stability prediction using the Hückel-Method. It took some time until the first purification were successfully made by Kroto, Smalley and Curl in 1985. For their method they used the conditions been present in a starformation as role model. Fullerenes were named after non of these physician. The name was taken from the architect Richard Buckminster Fuller who designed buildings in a similar shape like fullerene.

2 Nomenclature

Regular names of fullerene are too long and too difficult, so it was decided to just give the essential structural characteristics symmetrie without the information about the links between the circles. The name also includes the number of carbon atoms and the type of the circles.

3 General properties

Fullerene crystals have an brown/black metallic gloss. Their broad absorption spectra has a peak in the ultra violet and ends after the visible light region in the low infrared. After Eulers formation rules the number of carbon atoms in a fullerene must be $2(n+10)$. The least tension are present for pentagons surrounded by hexagons (isolated pentagon rule), where the pentagons are responsible for the bending. For a completely closed polyhedron there are at least 12 pentagons necessary.

4 $C_{60}$

4.1 Structure

$C_{60}$ is a point-shaped descret molecule with no 3-D structure in space. Its 12 pentagons are surrounded by 20 hexagons. This leads to the lowest pressure. Because of that $C_{60}$ is the most important fullerene and also the simplest to purify. $C_{60}$ has a diameter of 0.7 nm.

4.2 Electronic properties

Similar to graphite fullerenes have a sp$^2$ configuration where the $\sigma$ bonds, which are parallel to the surface of the sphere, form the structure. The bond length is similar to graphite, but the binding frame is not exactly 120°. Therefore there are less overlapp of
neighboring $\sigma$ orbitals which leads to less binding strength and an exact hybridisation of $sp^{2.278}$.

The $\pi$ bonds are perpendicular to the surface of the sphere and define the electronic properties. They form a electron cloud surrounding the carbon cage with an diameter of 1.05 nm.

### 4.3 Moleculecrystal and doping

At room temperature $C_{60}$ molecules form an Fcc-structure through Van der Waals Interaction. This configuration is a semiconductor with a bandgap of 1.5 eV. Metallic conductivity could be reached through doping. With the three times degenerated LUMO it is possible to get up to hexaanions. The new properties are dominated by the band-structure of the undoped matrix lattice and the valency of the donor. This leads to isotopic properties of the the surface.

### 5 Production methods

The small amounts of fullerenes produced with the first production methods could just be detected spectroscopically. This changed in 1990 with ”The Krätschmer-Huffman Arc-Discharge”.

#### 5.1 Krätschmer-Huffman-Method

The Krätschmer-Huffman Arc-Discharge consists of evaporating graphite electrodes via restrictive heating in a helium atmosphere. The resulting soot contain a few percent of fullerenes which could be extracted with benzene as solvent. This was the wirst method to produce gram-sized samples. The method was later on modified by Smalley who established an electric arc between two graphite electrodes, where most of the power dissipate in the arc. This modification granted higher yields. Due to these developments a lot of new fullerene families were discovered within the next years.

#### 5.2 Mass production: The Combusting Process

The common used process for mass-production is the ”Combusting Process” which was invented by Howard in 1991. In this process fullerenes are produced in sooting flames with premixed benzene, oxygen and argon under low pressure. The relativ low percentage of 0.26% of fullerenes in the soot was increased by some changes in the conditions up to 20% in 2002 when mass production of fullerenes started.

### 6 Endohedral Fullerenes

Fullerenes within atoms or clusters are called endohedral fullerenes. Since the purification of $La@C_{82}$ in 1991 a lot of new encaged species were produced. Nowadays it is possible
to produce fullerenes within e.g. metals, gas molecules or metallic nitride clusters. The interaction between these encaged species and the cage grants unique electronic structures. Therefore chemical functionalisation for application is a big goal. One of the important endohedral fullerenes are the metallofullerenes (EMFs). Metal ions could stabilise the cage structure (through charge transfer) of fullerenes which cannot be obtained in their empty form. They also influence the chemical properties e.g. the reactivity and regioselectivity.

6.1 Synthesis, separation and purification

Endohedral fullerenes are produced through chemical or physical processes. One of them is a modification of the already mentioned "DC Arc-discharge Krätschmer-Hoffman" method. Therefore the graphite rods are packed with metal oxides and some gases are added to the helium atmosphere. Due to the limited percentage of each fullerene species and the similar chemical properties of structural isomers it is challenging to separate the hugh amount of different fullerenes. The most common way to do this is called High Performance Liquid Chromathography (HPLC) which seperates the fullerene by weigh, size, shape and polarity.

7 Application

7.1 Superconductivity

Superconductivity in fulleren compounds were first observed in K$_3$C$_{60}$ with a $T_C$ of 18 K. The highest transition temperature was found as 33 K in Rb$_2$CsC$_{60}$. This is higher as in organic or intermetallic compounds, what makes superconductivity in fullerene compounds so interesting. The transition temperature $T_C$ is linked to the lattice expansion through doping. Therefore $T_C$ becomes a function of the intermolecular distance d. Through the appearing $^{13}$C-isotop effect the origin of the superconductivity is weak Electron-Phonon-Coupling. By ploting the magnetization as a function of temperature it was found, that fullerene compounds are hard Typ-II superconductors with no dissipation of vortices. Due to this a technical application is possible.

7.2 Ferromagnetism

In different C$_{60}$ compounds appears ferromagnetism below 20K. Searching for superconductivity it was found, that for polymerisation of C$_{60}$ under high pressure and high temperature the generated rhombohedral lattice provides (small) ferromagnetism at roomtemperature with a Curie-Temperature of 500 K. This compound was the first organic ferromagnet at roomtemperature. The advantages, in comparison with other ferromagnets, are the lightness of the material and the low rough material costs.
7.3 Organic photovoltaic

Fulleren-polymer-composition can be activated through light where the polymer acts as a donor and the fullerene as an acceptor. Due to low reorganisation energy for electron transfer reactions and good charge delocalisation fullerene are suited very good for organic photovoltaic. Also these compositions are light and cheap to produce. Therefore and due to the good processability the development was stimulated in the last years.

References


[8] Bob Yirka. „Simulation shows it’s possible to move H2O@C60 using electrical charge“. Physical Review Letters. April 22, 2013