Lecture 2. Physical Properties of Fullerenes. Chemical Properties and Reactions of Fullerenes

The purpose of the lecture: to provide information on the physical and chemical properties and reactions of fullerenes.

Expected results: to know the physical and chemical properties and reactions of fullerenes.

Physical Properties of Fullerenes

Fullerenes are extremely strong and resilient molecules with high bulk modulus and high impact strength. The fcc crystals of C60, held together only by van der Waals forces, are as soft as graphite. Theoretical calculations suggest that the effective bulk modulus of a single C60 buckyball molecule is 668 GPa when compressed to 75% of its size in the closest packing of the crystals in the fcc lattice. This property makes fullerenes become harder than steel and diamond, whose bulk moduli are 160 GPa and 442 GPa, respectively. Fullerenes are extremely strong molecules, able to resist great pressures —they will spring back or bounce back to their original shape and normal volume when the pressure is relieved after being subject to over 3000 atmospheres. Ion beam scattering experiments demonstrated the exceptionally high stability of fullerenes with respect to impactinduced fragmentation processes thus predicting high resilience for these molecules.

The fullerene C60 has remarkable impact strength being able to withstand high-speed collisions of up to 15,000 mph against stainless steel plate, merely bouncing back, unharmed, keeping their shapes, thus showing high stability.

Chemical Properties and Reactions of Fullerenes

The electronic structure of C60 shows that the HOMO is completely occupied and there are three low-lying degenerate LUMOs. Thus C60 is more of an electron acceptor (electrophile) than an electron donor. C60 can readily accept six additional electrons that can go into the three degenerate LUMOs. The C60 fullerene has just the right combination of size, chemical stability, and activity to serve as the building block for a large variety of solids with fascinating properties.

Metal-Doped Fullerenes

One of the most interesting properties of solid C60 or the bulk C60 are the electronic properties, where in various forms it can act as an insulator, conductor, semiconductor, or a superconductor. Metal-doped fullerenes are the first three-dimensional organic electrical conductors. Metal-doped fullerenes are solids that involve metal doping in the interstitial holes within the lattice of solid C60.

The fcc lattice of C60 has octahedral and tetrahedral holes within the lattice, which can accommodate metal atoms to form metal-doped solids known as fullerides.

The process of metal doping in interstitial holes, also called metal intercalation, involves charge transfer from donor metal to acceptor C60. Vapor phase diffusion is one of the most important methods to prepare metal-doped C60. Metal doping or intercalation of C60 with alkali metals provides a way to alter the electronic properties of fullerenes since the smaller alkali metal ions should be able to fit into the interstices in the lattice without disrupting the network of contacts between the carbon spheroids. Solid C60 is a semiconductor. The addition of three electrons (half-filling) to the degenerate LUMO by exohedral metal doping with potassium leads to an fcc K3C60 structure that is an electrical conductor at higher temperatures but is a superconductor at 18 K.

Figure 1 shows the structure of metal-doped C60 (K3C60) with potassium ions filling the single octahedral hole and the two tetrahedral holes per C60 as per the stoichiometry requirements for fcc lattice. Both C60 and K3C60 correspond to fcc lattices of nearly identical unit cell size: 14.11 A for C60 and 14.24 A for K3C60. Potassium buckide, as it is also called, with potassium ions filling the cavities between the buckyballs, is a stable metallic crystal and the first completely three- dimensional molecular metal. The addition of six electrons by external doping yields the bcc (body-centered cubic) structure K6C60 that has poor electrical conductivity. In general, for the alkali metals A (Li, Na, K, Rb, Cs) only A3C60 fcc exhibits superconductivity. The A6C60 bcc exhibit poor electrical conductivity. The superconducting temperature can be increased to 28 K when using Rb and can be further increased to 33 K by using Cs and Rb together. A superconducting temperature of 40 K has been reported for Cs-doped C60.

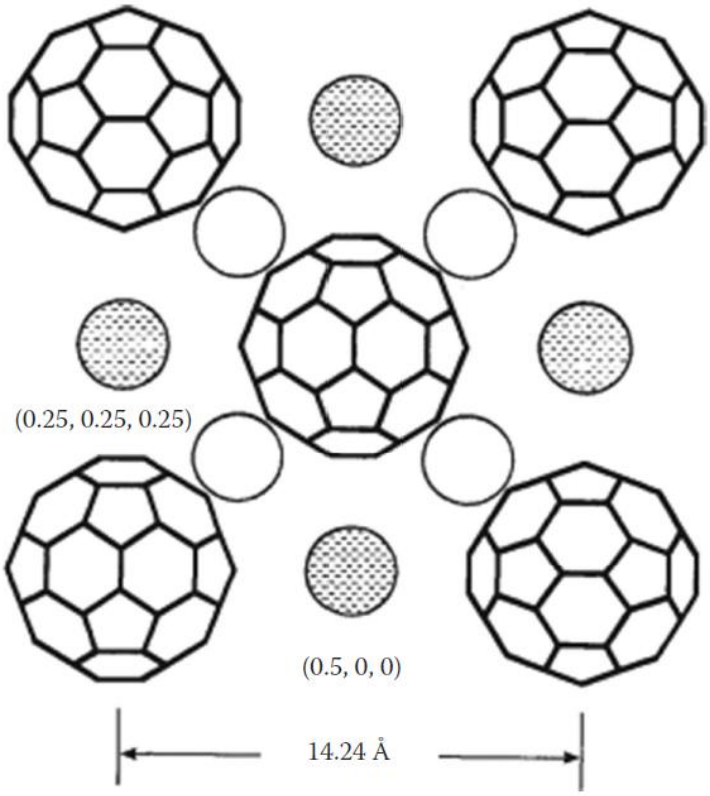

FIGURE 1. Structure of metal-doped C60 (K3C60). The open (0.25, 0.25, 0.25) and hatched (0.5, 0, 0) spheres represent the potassium at the tetrahedral and octahedral sites, respectively.