CHAPTER 1

INTRODUCTION

The discovery of a new form of carbon – the carbon cage molecules C_N, called fullerenes, by Smalley, Kroto and co-workers [KHB85] has led to a new class of carbon-based solids which exhibit a wide variety of unusual physical and chemical properties. The most stable member of the fullerene family, C_{60}, was named "Buckminsterfullerene", giving reference to the architect of geometric domes, Buckminster Fuller. The breakthrough in the research of fullerene properties came only after the discovery of the electric arc production and the solubility in toluene for the extraction of C_{60} (and C_{70}) from soot in gram quantities by Krätschmer et al. [KLF90]. Recently, a chemical method was developed for the synthesis of the smallest fullerene C_{20} [PWL00].

The C_{60} molecule has an icosahedral (I_h) symmetry, with 120 point group operations for the 60 carbon atoms located at the corners of the 20 hexagonal and 12 pentagonal faces of a truncated icosahedron. In the pristine solid state, the molecules organise in an fcc lattice with a nearest neighbour distance of 10.02 Å. The molecules rotate freely about their lattice positions at room temperature. Crystalline C_{60} is an almost ideal molecular solid, with very weak Van der Waals intermolecular interactions. Covalent bonding between the molecules can be induced under special conditions, such as photoirradiation, exposure to high pressure and high temperature or ion irradiation, leading to the formation of C_{60} polymers [EkR00]. The polymerised C_{60} is not soluble in toluene, in contrast to the pristine material. Photolithographic applications for fullerene films were considered [HEF93]. Although much work has been dedicated to the study of the photopolymerised C_{60}, there are still open questions regarding the mechanism of the photopolymerisation, the early stages and the onset of photopolymerisation in thin film and bulk material.

In this thesis, a highly sensitive optical method, second harmonic generation, is used in combination with infrared spectroscopy to study the photopolymerisation process at low irradiation doses in thin films of C_{60}. Several studies were made under ultra high vacuum conditions. The results of this work are presented in Chapter 2.

The unique structure of fullerenes allows for different types of doping, i.e. endohedral doping, where the dopant is inside the fullerene cage, substitutional doping, with the doping atom replacing a carbon atom in the fullerene shell and exohedral doping, with the dopant sitting outside or between the fullerenes. The interest in fullerenes and their doped compounds has been particularly stimulated by the discovery that films of C_{60} doped exohedral with alkali atoms are conducting at room temperature [HHR91]. The discovery that the K_3C_{60}, Cs_3C_{60}, Rb_3C_{60} and $Cs_xRb_yC_{60}$ phases became superconducting at temperatures of 18 – 33 K was even more exciting [HRH91, TES91, KCL91]. Superconductivity up to 117 K has been published recently for hole-doped lattice-expanded C_{60} [SKB01]. However, all these compounds are unstable in air. Encapsulation of the metal atoms came in view as this could lead to an increased chemical stability of the compounds.

Endohedral $Li@C_{60}$ was the first alkali-metal endohedral fullerene synthesised in macroscopic quantities [TKL96, Tel97]. The molecule can be efficiently separated from C_{60} and chromatographically purified to a 95% content of endohedral molecules over C_{60} [Kra98]. Chapter 3 of this thesis presents our investigations on different properties of this molecule in the solid state. Thin film deposition conditions, the optical properties of the vapour-deposited films and the phototransformation will be discussed. First evidence for photopolymerisation of endohedral fullerenes is given. A first study on the relaxation dynamics of excitons in films of $Li@C_{60}$ is presented.

The discovery of fullerenes and the confirmation of their icosahedral structure have given new insights into the physics of carbon fibers. Although hollow carbon tubules were known to form the core of relatively thick (in the micrometer range) carbon fibers, it was only in 1991 that S. Iijima proposed a simple geometrical structure for these tubules, thereafter called carbon nanotubes, as perfectly graphitised closed seamless shells. Carbon nanotubes are expected to have unique features, such as optical and electronic properties, which are very sensitive to their geometry and dimensions [Ebb97]. Despite the very fast development in the production of carbon nanotubes in the latest years, only a few studies on their nonlinear optical properties have been reported in the literature. The separation of specific types of carbon nanotubes, metallic or semiconducting with selected diameters or the selected growth of nanotube crystals has just come into sight [SSG01]. The nonlinear optical properties are, in particular, expected to be very interesting in ordered films of these quasi one- dimensional structures. A new high harmonic generation mechanism has been proposed by Slepyan et al. [SMK99, SMK01]. The interaction of high-intensity lasers with samples of aligned multiwall carbon nanotubes is described in Chapter 4 of the present work.

A summary of the results is presented in Chapter 5.