CONTENTS

CHAPTER 5

SUMMARY

Different properties of novel carbon materials have been investigated, mainly using non-destructive optical linear and non-linear methods.

Second harmonic generation (SHG) of the fundamental wavelength of a Nd-Yag laser (1064 nm) was applied for the first time to study the phototransformation of fullerene materials. The method was shown to be very sensitive to the initial phase of photopolymerization of C_{60}. Photopolymerization with less than 10^{20} photons/cm^2 from an Ar^+ laser at 514.5 nm, first indicated by SHG measurements, was also confirmed with infrared absorption (IR) spectroscopy. This dose is about two orders of magnitude lower than the dose previously reported from Raman spectroscopy. The presence of both dimeric and polymeric modes in the IR spectra of films irradiated with very low doses suggests an oligomerisation scenario around nucleation centers, which refer to the structures described by the X-ray diffraction work of Pusztai et al. [POF99]. The structure of the crystalline films, probed with the SHG anisotropy, was not significantly affected in these early stages of polymerisation. The thickness threshold behaviour for the onset of the polymerisation found in this work is in good agreement with the Raman spectroscopy measurements of Park et al. [PHK98]. We can explain this behaviour, based on a mechanism, in which the polymerisation reaction is promoted by the self-trapped state of the charge transfer excitons.

Detailed investigations of the thermal stability and sublimability of the endohedral fullerene Li@C_{60} were made using thermal desorption spectroscopy (TDS), laser desorption mass spectroscopy (LDMS) and solubility tests combined with chromatography (HPLC). The molecule can be deposited as thin films by sublimation at high heating rates. The optical properties of vapour-deposited films of Li@C_{60} have been studied. The IR spectra measured from these films are in good agreement with the theoretical predictions for an endohedral structure of the molecule. The dimer fraction (Li@C_{60})$_2$ forms a semiconducting molecular solid with a bandgap of 1.06 eV, which was deduced from the ultraviolet- visible (UV-VIS) absorption spectrum. A strong absorption centered at 1.1 eV measured from vapour-deposited films of the Li@C_{60} monomer gives evidence for an intramolecular charge transfer from the Li 2s orbital to the LUMO of the fullerene cage. The absorption peaks in these solid materials are broadened and red-shifted compared to their absorption in solutions, which is indicating a strong intermolecular interaction in the solid state.

A first study of the dynamics of excitons in an endohedral material is presented here. The transient bleaching of the absorption at ~ 1 eV for Li@C_{60} compared to an induced absorption in C_{60}, following the excitation with photons of 1.98 eV is another experimental evidence for the intramolecular charge transfer in Li@C_{60}. A higher mobility of the excitons in Li@C_{60} and (Li@C_{60})$_2$, compared to C_{60}, can be deduced from these measurements, which indicates a strong intermolecular interaction, leading to a larger delocalisation of the electronic states in the solid.

Li@C_{60} is the first endohedral fullerene shown to undergo a process of photopolymerisation. The transformation kinetics is biexponential with irradiation dose constants 0.4 and $5.7 \cdot 10^{20}$ photons/cm^2 similar to C_{60}, which indicates the relevance of a 2+2 cycloaddition scheme for the polymerisation of Li@C_{60}. Photopolymerisation was confirmed based on solubility tests in oDBC solvent, IR spectroscopy and TDS measurements.

The interaction of high-intensity lasers with CNTs mainly results in the generation of a broad optical continuum, tentatively explained based on the production of free electrons, which are exciting a non-destructive plasma in air. More investigations are needed to clarify this process. The evident high efficiency of electron emission under the action of light recommends CNTs as pulsed electron emitters. Measurements of the third and fifth harmonic generation revealed that the semiclassical theory predictions concerning the high harmonic generation in carbon nanotubes fails to describe the behaviour of semiconducting tubes. This is in good agreement with the results calculated with a full quantum-theoretical model [SMK02].