

## Chapter 4

### Conclusion

#### 4.1 Conclusion

This dissertation presented detailed nonlinear optical studies performed on specifically chosen novel fullerene materials. Firstly, we described the wavelength dependence of the optical limiting measurements on solutions of higher cage fullerenes ( $C_{70}$ ,  $C_{76}$ , and  $C_{84}$ ) and the derivatized fullerenes ( $C_{60}$  secondary amine,  $C_{60}$  cyclic ketone,  $C_{60}(C_8H_6O_2)$ , and  $C_{60}(C_{10}H_{14}O_4)$ ). Our measurements concentrated on the proven main optical limiting mechanism for  $C_{60}$ : reverse saturable absorption. We examined the critical relationships between the wavelength dependences of the ground and excited state absorptions. We also used the optical limiting data to calculate the triplet-triplet excited state absorption cross-sections for two of the materials. The results demonstrated that the optical limiting effect of  $C_{60}$  can be further extended in the near infrared regime by appropriate modifications of the molecular structure of  $C_{60}$ . Thus, we showed that the higher cage fullerenes and the derivatives are better optical limiters for wavelengths higher than 650 nm. This wavelength is considered as a "cut-off" value of the optical limiting effect for  $C_{60}$ , because beyond it, the ground state absorption of the molecule becomes too weak. Although the excited state

absorption cross-section has a maximum at 700 nm, the excited states can not be accessed, and so the optical limiting effect is substantially reduced.

Wavelength dependent optical limiting measurements on  $C_{76}$  solution in toluene showed that this molecule is a better optical limiter than  $C_{60}$  beyond 650 nm and up to 800 nm, with its best performance around 750 nm. For wavelengths higher than 800 nm the material is still limiting but not as strong.

The  $C_{84}$  solution in  $\alpha$ -chloronaphthalene showed a weak optical limiting effect in the range 800-880 nm. For the first time, we performed optical limiting measurements on five individually separated structural isomers of  $C_{84}$  in  $CS_2$ . These materials were available to us in very small amounts, so the measurements were done only at the wavelength 600 nm. Nonetheless, we obtained intriguing results which showed that the dominant isomer, labeled A, is not the one that has the strongest optical limiting effect. Rather, the next abundant isomer, B, exhibited the strongest reverse saturable absorption. In fact, isomer A is one of the weaker optical limiters of the isomers isolated and studied so far.

As a result of the symmetry breaking of the fullerene sphere, the derivatized fullerenes also showed improved optical limiting effect at wavelengths higher than 650 nm compared to  $C_{60}$ . The first series of experiments used  $\alpha$ -chloronaphthalene as a solvent. Despite the limited input energies imposed by decomposition of the solvent, the derivatives showed exceptionally strong optical limiting up to 750 nm, with results even better than  $C_{76}$  at 700 nm, for the same low intensity transmission. Beyond this wavelength, the  $C_{60}$  derivatives become transparent, and no optical limiting is observed.

Because each of the  $C_{60}$  derivatives displayed similar behavior, we further studied only  $C_{60}$  cyclic ketone in a different solvent,  $CS_2$ . The purpose of the

study was to increase the input energies from 50  $\mu\text{J}$  up to 300  $\mu\text{J}$  to obtain an increased dynamic range. By careful calibration of the concentration, we determined the ground state and excited state absorption cross-sections in the 640-735 nm range. We concluded that  $\text{C}_{60}$  cyclic ketone has an excited state absorption peak around 700 nm, which is shifted from the 750 nm value for  $\text{C}_{60}$ . The shift in the excited state absorption cross-section of the derivatives is the result of the attachment to the  $\text{C}_{60}$  molecule of different chemical groups.

Secondly, we performed the first degenerate four-wave mixing experiments on an endohedral metallofullerene,  $\text{Er}_2@\text{C}_{82}$ . We showed that the charge-transfer from the encapsulated atoms to the empty cage increases the third order nonlinear susceptibility,  $\chi^{(3)}(-\omega; \omega, \omega, -\omega)$ , by more than two orders of magnitude compared to that of the empty cage fullerene. The enhancement in the nonlinear optical properties of the endohedral metallofullerenes is due to the charge transfer from the dopant atom(s) to the empty cage. This process is similar to the optical excitation of the empty cage fullerene. The main advantage in the case of the ground state charge transfer in endohedral metallofullerenes is the fact that one does not need to optically excite the material to benefit from the large nonlinearities present in the medium. From our measurements on  $\text{Er}_2@\text{C}_{82}$  in  $\text{CS}_2$  solutions, we determined the value for the second order hyperpolarizability,  $\gamma_{xyyx}^{(3)}(-\omega; \omega, \omega, -\omega)$ , to be  $-8.65 \times 10^{-32}$  esu. This value was used to estimate the third order nonlinear susceptibility  $\chi_{xyyx}^{(3)}$  for a pure  $\text{Er}_2@\text{C}_{82}$  film to be  $1.1 \times 10^{-9}$  esu. For comparison, the value found in the literature, for orthogonal polarizations, was  $\chi_{xyyx}^{(3)} = 1 \times 10^{-12}$  esu, measured for both  $\text{C}_{60}$  and  $\text{C}_{70}$  films, which corresponds to  $\gamma_{xyyx}(-\omega; \omega, \omega, -\omega) = 4 \times 10^{-35}$  esu for  $\text{C}_{60}$ . We also performed DFWM measurements on the empty cage fullerene  $\text{C}_{82}$  and observed

that the DFWM signal for the empty cage fullerene was indistinguishable from that of the pure solvent, thus indicating that the value for  $\chi_{xyyx}^{(3)}(-\omega; \omega, \omega, -\omega)$  is expected to be much smaller than the value for  $\text{Er}_2@\text{C}_{82}$ .

## 4.2 Future Work

For a more complete analysis of optical limiting in fullerene materials, the higher cage fullerenes as well as the derivatives, it is recommended to perform transient excited state experiments on these materials, in order to determine the triplet-triplet excited state absorption cross-sections, and compare the results with the values determined through our optical limiting measurements. These measurements would also provide the full spectrum of the triplet-triplet absorption. For the same purpose, optical limiting experiments in which picosecond laser pulses are used will allow for a methodical analysis of the singlet excited state absorption cross-sections. This experiment is possible because the inter-system crossing  $S_1 \rightarrow T_0$  takes place on time scales of one nanoseconds. Considering that for practical purposes the fullerene materials can not be used as easily in solution form, the optical limiting experiments would offer valuable information if they will be also performed on films. This requires more material of each of the structures.

In the case of the DFWM experiments on  $\text{Er}_2@\text{C}_{82}$ , work is currently in progress on experiments in which picosecond laser pulses are used on films made with the same material. This route is more advantageous, as we expect to obtain a

higher phase-conjugate signal, since more material is incorporated in the film and a higher intensity is provided by the picosecond laser beam.

As other endohedral metallofullerenes become available, it is important to look at how the third order nonlinear susceptibility varies with the size of the cage and also how it varies with the number of dopant atoms for the same cage size. Furthermore, another important study is to examine the wavelength dependence of the third order nonlinear optical susceptibility,  $\chi^{(3)}(-\omega; \omega, \omega, -\omega)$  in these novel endohedral metallofullerenes charge transfer systems.