SPECTROSCOPIC STUDIES ON C_{60} FULLERENE SOLUTIONS IN BINARY SOLVENT MIXTURES

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Abstract. Correlated studies of UV-VIS absorption spectroscopy, Surface Enhanced Raman Scattering (SERS) and photoluminescence (PL) evidence the aggregation of C_{60} in binary solvent mixtures. The C_{60} self-assembling process depends on the strength of the interaction forces. The aggregation process was studied in o-dichlorobenzene(DCB)/acetone (AC) and DCB/N-methyl-2-pyrrolidinone (NMP) solvent mixture.

Key words: Fullerene, UV-VIS absorption, SERS, PL, binary mixtures.

1. INTRODUCTION

C_{60} fullerene dissolved in single solvents or in binary solvent mixtures exhibits inciting properties due to the formation of aggregates [1–8]. In general, these formations are very unstable, even at mechanical disturbances [2, 4] or small increase of temperature.

In the binary liquid mixtures, consisting in a strong fullerene solvent and a poor one, the aggregates are more stable at mechanical disturbances [1]. Due to the mildly electrophilic character, C_{60} can also form charge transfer complexes with nucleophilic solvents such as N-methyl-2-pyrrolidinone (NMP). These complexes have a strong tendency of self-assembling in aggregates with solvent molecules bound within.

In the present work, we have used the UV-VIS optical absorption and Surface Enhanded Raman Scattering (SERS) to examine the aggregation of C_{60} in two binary solvent mixtures: o-dichlorobenzene (DCB)/acetone (AC) and DCB/NMP. The first mixture consists in a strong and a poor fullerene solvent, respectively. The second mixture contains a solvent-like NMP, which may act both as a solvent and as a reactant regarding C_{60}. Also, in this case, the photoluminescence (PL) studies have evidenced the changes which occur in the aggregation process over a long storage time of the solutions.

2. EXPERIMENTAL

The solvents, DCB, AC, NMP and C_{60} powder used in this work were Merck products. Solutions with different concentration of C_{60} in the range of 0.2–2 mg/ml were prepared by dilution starting from a solution with a content of C_{60} of 2 mg/ml. After preparation, the solutions were ultrasonically homogenized for a few minutes and hermetically bottled in quartz cells. The UV-VIS absorption, SERS and PL measurements on solutions samples were performed at room temperature. Also, for the SERS studies C_{60} films were used prepared from fresh solutions, *i.e.*, just after dissolving of C_{60} and from solutions left standing in the dark for different times.

SERS studies were performed at room temperature in a backscattering geometry, under excitation wavelengths at 1064 nm, using a FT Raman Bruker RFS 100 spectrophotometer. The measurements were carried out on films, of ~ 100 nm thickness deposited on Au supports with a rough microstructure in the range of 10–100 nm.

The PL records were obtained in a backward geometry using a computer controlled emission spectrometer consisting from a SPEX double monochromator equipped with a cooled EMI photomultiplier and a photon counting system. Laser line of 457.9 nm from Coherent Innova 90 argon ion laser was used as excitation light.

3. RESULTS AND DISCUSSION

Put together, DCB and AC, form a typical solvent mixture, with different dissolving properties against C_{60}, which favours an intense polydisperse aggregation of fullerene. The same as in a precipitation process, clusters of C_{60} of different size are yielded. Changing both the weight ratio of the solvent/non-solvent and concentration of the fullerene one varies the rapidity of the aggregation process and the clusters size which grows slowly if the solution is left to stand for a longer period of time. Specific for this self-assembling of C_{60} is an unusual solvatochromism, featured by an abrupt variation of the absorbency, appearing at a critical concentration of the poor solvent in the solvent mixture (Fig. 1a). The whole process being driven by van der Waals forces, the weak interactions between packed particles do not change their individual properties. This is shown in Fig. 1b, where despite of significant variations in the absorption spectra, indicating the formation of aggregates, the SERS spectra do not vary, remaining similar with the isolated fullerene. The presence of the band at ~ 343 cm^{-1}, discussed in [9] is the main evidence that in these aggregates C_{60} behaves as isolated fullerene.

As we mentioned above, NMP acts both as a solvent and the reactant. Due to the unpaired electrons of the amide nitrogen atom, the NMP molecule is particu-

Fig. 1 – Absorption (a) and SERS (b) spectra of C_{60} dissolved in (o-dichlorobenzene/ acetone) mixtures. From bottom to top are displayed the absorption spectra of 0.04% wt C_{60} in (o-dichlorobenzene/ acetone) mixtures of percentages (100 + 0), (83.3 + 16.7), (66.7 + 33.3), (50 + 50), (33.3 + + 66.7) and (16.7 + 83.3). SERS spectra were recorded at 1064 nm excitation wavelength on films of about 100 nm deposited by evaporation of the solvent on Au supports of comparable roughness.
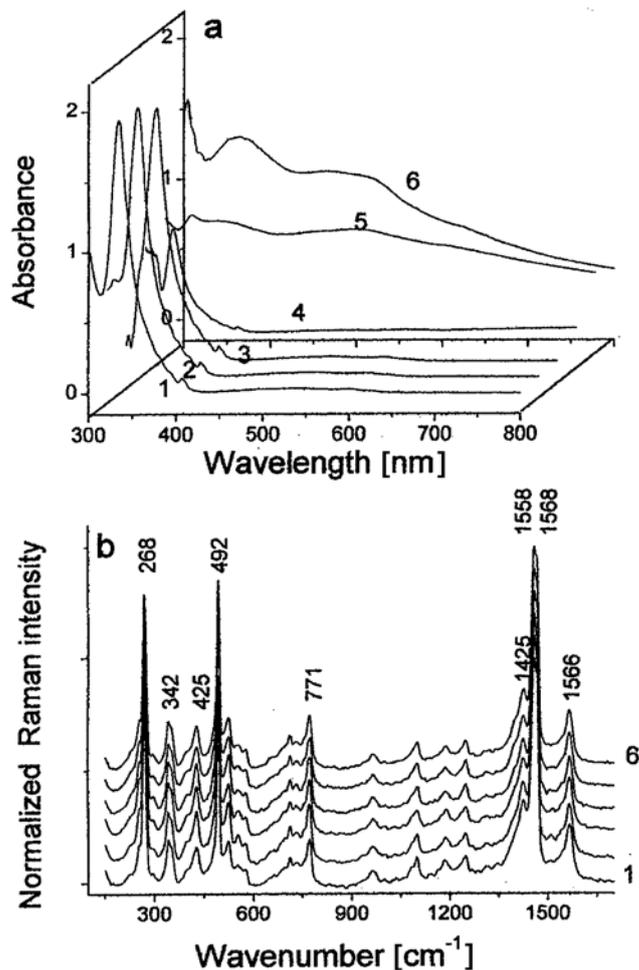
larly reactive against C_{60}. By binding the pyrrolidinone ring to fullerenes cage, molecular complexes (C_{60}, NMP) are formed that aggregate slowly. Such an interaction is brought to view by the UV-VIS absorption spectra of C_{60} in solvent mixtures of DCB/NMP in Fig. 2.

The charge transfer between fullerene as an acceptor and NMP molecule as a donor, leading to molecular complexes (C_{60}, NMP), is put into evidence in Fig. 2a by a gradual modification of the absorption spectra with the increase of the NMP weight in the solvent mixture. As in any C_{60}-derivatives, the interaction with NMP lowers the molecular symmetry of C_{60}, which in turn modifies both the phonon and electronic spectra. Fig. 2a referes to the transformation of the C_{60} from a high symmetry degree featured by weakly allowed low-lying electronic transition, as for C_{60} dissolved in DCB, into a lower molecular symmetry which increases the absorption
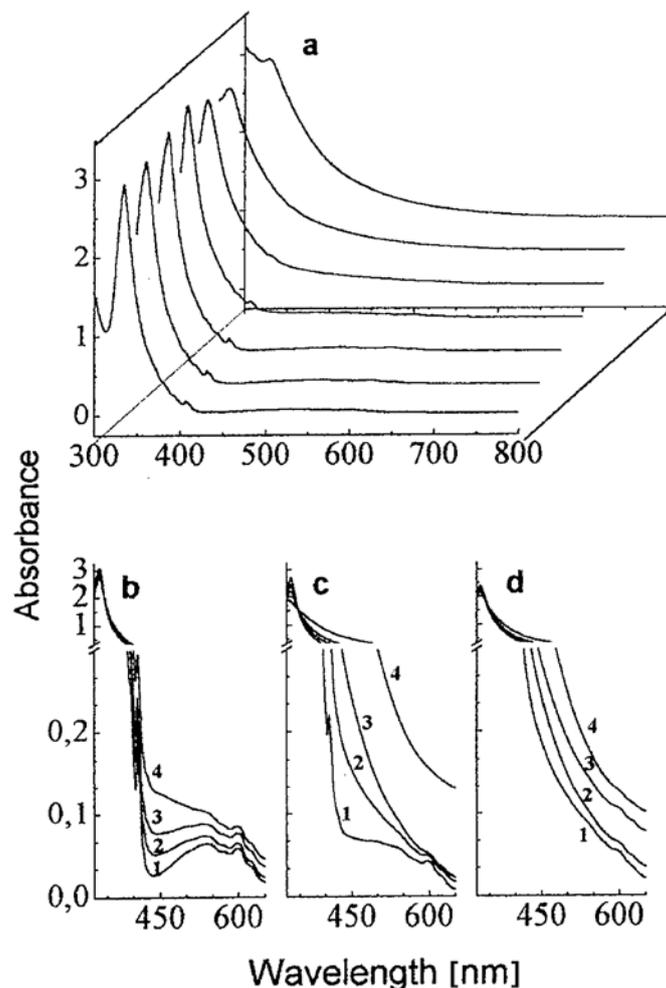
Fig. 2 – Absorption spectra of C_{60} in (o-dichlorobenzene/N-methyl-2-pyrrolidinone) mixtures (a), from bottom to top are displayed the absorption spectra of 0.04% wt C_{60} in mixtures of percentages (100 + 0), (91.6 + 8.4), (83.3 + 16.7), (66.7 + 33.3), (50 + 50), (33.3 + + 66.7) and (16.7 + 83.3). The figures (b), (c) and (d) show the variation of the absorption spectra with the storage time for the solutions made in the solvent mixtures of percentages (91.6 + 8.4), (83.3 + 16.7) and (50 + 50), respectively; curves 1, 2, 3 and 4 correspond to the initial state and to a storage time of 5, 10 and 30 days, respectively.

of the ground-state of C_{60} existing in the (C_{60}, NMP) complex. Later on, the isolated and small clusters of (C_{60}, NMP) are slowly associating, forming large and stable aggregates. This explains the absence in the Fig. 2a, of an abrupt variation of absorbency like that occurred in the DCB/AC mixture.

The whole process, resembling to a crystallization from a liquid phase, evolves continuously slower or faster depending on the relative concentration of the two reacting components. It is well illustrated in Fig. 2b-d by a variation of absorbency if the solutions are left standing for longer time.

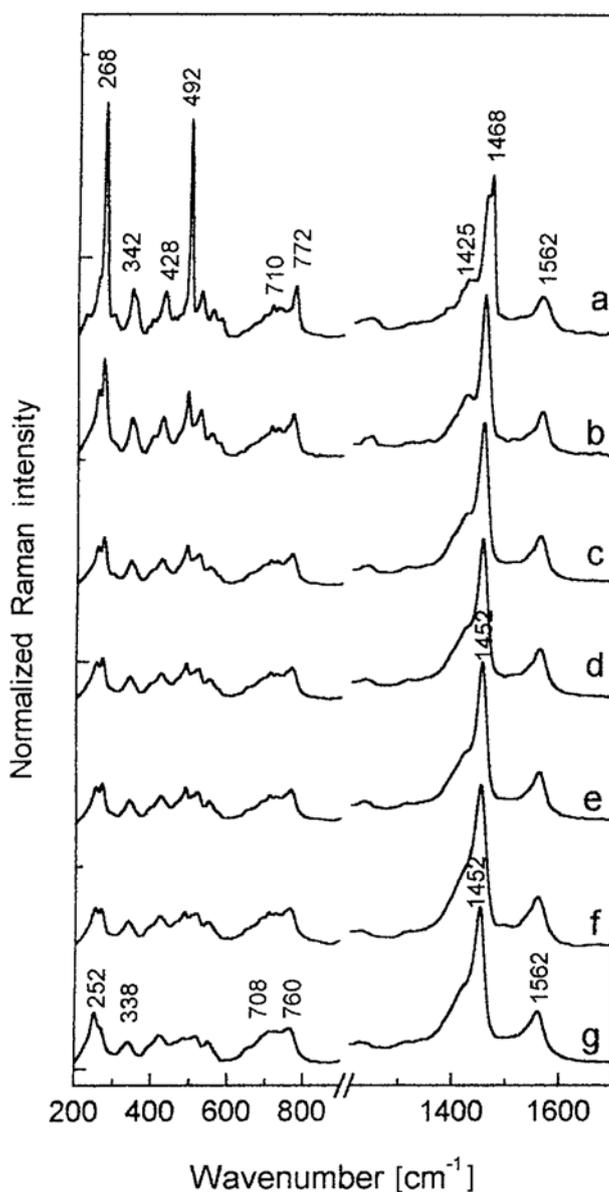Fig. 3 shows the SERS replica of Fig. 2a after one storing day of the solution.

Fig. 3 – SERS spectra at 1064 nm excitation wavelength on C_{60} films deposited on rough Au substrate from a solution of 0.04% wt C_{60}, prepared in (o-dichlorobenzene/N-methyl-2-pyrrolidinone) mixtures. Spectra a, b, c, d, e, f and g, respectively, correspond to the mixtures of percentages (100 + 0), (91.6 + 8.4), (83.3 + + 16.7), (66.7 + 33.3), (50 + 50), (33.3 + 66.7), (16.7 + 83.3), respectively. All spectra were recorded on films of ~ 100 nm thickness prepared from solutions stored one day.

One sees immediately that the presence of NMP changes dramatically the Raman spectrum of C_{60}. As a main characteristic, we notice the strong decreasing of the Raman bands intensity associated to the radial vibration modes. The most relevant is the band at 269 cm^{-1} associated to the H_g (1) vibration mode. As a specific fact, one observes that by the increase of NMP weight in the solvent mixture a new band at ~ 225 cm^{-1} appears, as a down shifted replica of H_g (1) band, which becomes one of the most intense Raman bands in the spectral range below 600 cm^{-1}. At the same time, the Raman band associated to the A_g (2) band exhibits an asymmetric profile peaked at ~ 1452 cm^{-1}. The band variation is due to a lowering of symmetry, produced by the interaction of C_{60} with the NMP molecules. The lowering of symmetry has a permanent character and it is related to the stability of the (C_{60}, NMP) complexes.

It is known that by the symmetry reduction new lines previously forbidden are activated in the IR and Raman spectra and multiple splitting of some allowed modes bands appear, while the intensity of many original bands decreases. The new band appearing at ~ 255 cm^{-1} must be one of these. It is important to remark that this band is also found in the Raman spectrum of the C_{60} dimer. It may be considered as a component of the group of three bands, at ~ 275, ~ 254 and ~ 242 cm^{-1} formed by splitting of the H_g (1) vibration mode [10].

Drastic changes for the C_{60} dissolved in the DCB/NMP mixture are observed also in the PL spectra. To evidence the double role of the NMP molecules, solvent and reactant, we present for comparison the PL behaviour of C_{60} in neat DCB, an emission band with the peak position of about 1.77 eV typical of weak fluorescence of solvated C_{60} (Fig. 4a). If the solution was left standing longer period of time no relevant changes in the emission spectra were observed. This result shows that the formation of aggregates in this case involves just weak interball interaction, of van der Waals type, that cannot significantly alter the emission characteristics of C_{60}.

A different behaviour is observed with C_{60} dissolved in DCB/NMP mixture (Fig. 4b). The solution storage leads to a spectacular increase of emission intensity in PL spectra. After shorter storage time, the enhancement of PL intensity is accomplished especially by an emission in the red region (red band) with the peak position at about 1.92 eV. An additional emission situated in the green (green band) with the maximum at about 2.25 eV is observed after a longer storage time. These changes in PL spectra, deriving from interaction between C_{60} and NMP must be related to the nucleophilic properties of the NMP molecules. Slow development of the interaction explains the persistence in the emission spectra, for a longer period of time, of the band peaking at 1.77 eV attributed to the non-interacted C_{60} molecules.

Fig. 4 – PL spectrum of fresh prepared C_{60} solution in DCB with fullerene content of 0.4 mg/ml (a), in the inset the emission spectrum of DCB is shown. Fig. (b) shows the PL spectrum of C_{60} solutions in (o-di-chlorobenzene/N-methyl-2-pyrrolidinone) mixture with a volume ratio of 1:5. From bottom to top are presented the curves recorded on fresh prepared solution and stored for one and two years, respectively.
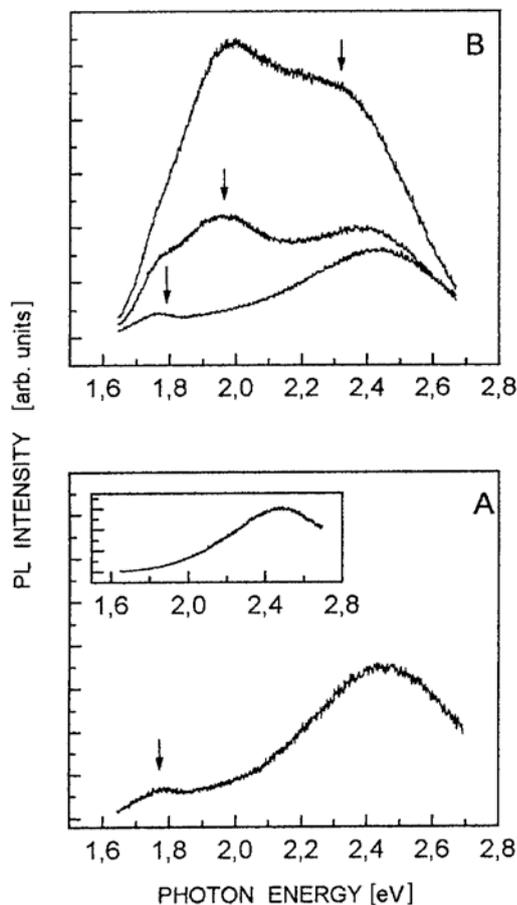
4.CONCLUSIONS

This paper reports new results concerning the aggregation of C_{60} in binary solvent mixtures. We have studied by UV-VIS absorption, SERS and PL the aggregates of C_{60} formed in DCB/AC and DCB/NMP mixtures.

In solvent mixtures, consisting in a strong and poor fullerene solvent like DCB/AC mixture, a polydisperse type aggregation of C_{60} is present, similar to a process of precipitation yielding clusters of C_{60} of different shape and size. Despite of significant variations in the absorption spectra and without reference to the aggregated state, the SERS spectra are similar between them and do not vary as those recorded on the C_{60} powder.

The behaviour of C_{60} in the DCB/NMP mixture, where the latter is a solvent with nucleophilic properties, is different. In this case stronger forces are present,

originating in the charge transfer from the solvent molecules, as electron donor, towards fullerene, as electron acceptor. The main SERS signature for the interaction between C_{60} and NMP is done by a new band at ~ 255 cm^{-1} which seems to replaces the original band at 269 cm^{-1} associated to the H_g (1) vibration mode. In the spectral range of the pentagonal pinch mode, an aymmetric A_g (2) band shifted at ~ 1452 cm^{-1} is also observed. The lowering of the symmetry in the parent I_h C_{60}, produced by the interaction with the molecules of the solvent is permanent and features the ground state of C_{60} bound in (C_{60}, NMP) complexes [9].

Also, the interaction between C_{60} and the NMP molecules from the DCB/NMP mixture is revealed by the PL spectra. It is noticed that the emission intensity increases gradually with the storage time of the solutions. Two emissions bands, red with the peak position at about 1.92 eV, and green with the maximum at about 2.25 eV, were identified. Because the band peaking at 1.77 eV associated with the non-interacted C_{60} molecules persists after a longer storage time of the solutions, the interactions between C_{60} and NMP develops at a slow rate.

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