

Dedicated to Acad. Prof. Dr. Margareta Giurgea with the occasion of her 90-th anniversary

SURFACE-ENHANCED RAMAN SCATTERING, PHOTOLUMINESCENCE AND VISCOSITY STUDIES ON C₆₀ AGGREGATES IN N-METHYL-2-PYRROLIDINONE

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Correlated studies of Surface Enhanced Raman Scattering (SERS) spectroscopy, photoluminescence (PL) and viscosity on aggregation of C₆₀ fullerene in N-methyl-2-pyrrolidinone (NMP) solutions were performed. The aggregation is a result of storing of the solutions at the room temperature for different periods of time. The modified phonon spectrum in the aggregate phase is a consequence of the intermolecular interactions that lead to a large reduction in parent I_h C₆₀ symmetry. The Raman range below 800 cm⁻¹ is the most diagnostic for aggregate assignment. Substitution of the original of H_g (1) band from ~269 cm⁻¹ with a new one at ~255 cm⁻¹ relates the formation of (C₆₀, NMP) complexes. In the second stage of aggregation, this band shifts at ~246 cm⁻¹ and a new band, associate to the interball interaction, is formed at ~94 cm⁻¹. PL emission of the C₆₀ solutes in NMP presents two components, one in red (1.92-2.00 eV) and another in green (2.18-2.3 eV), which originate in two successive processes. Their weights depend on C₆₀ concentration and on storage time. In the beginning are formed quickly molecular complexes (C₆₀, NMP) by charge transfer, which on associate slowly in stable aggregates. A dependence of specific viscosity on C₆₀ solution concentration is observed too.

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1. Introduction

One of the most interesting properties of solvated C₆₀ fullerene in single solvents and in solvent mixture is the self-assembling in nanometric size clusters [1-8]. Based on weak intermolecular van der Waals interactions, this property relates the polarizability of the interacting particle, whose magnitude determines the stability, with the size of C₆₀ fullerene clusters [8,9]. Due to the mildly electrophilic character [10,11], C₆₀ can also form charge transfer complexes with various organic electrons donors [12,13]. A special attention was paid to the complexes with aliphatic [14] and aromatic amines [15,16]. Moreover, C₆₀ is able to form molecular complexes not only with well-known electron donors but even with the solvent molecules [17,18].

In genesis of stable fullerene self-assemblies, the strength of intermolecular interaction solute-solvent plays an important role. As a result, some particularities of C₆₀ behavior are expected in nucleophilic solvents where beside the weak van der Waals type forces other stronger forces of chemical origin can act, in relation to a charge transfer between fullerene as acceptor and solvent molecules as donor. Solvent as N-methyl-2-pyrrolidinone (NMP) is particularly reactive against C₆₀ due to the unpaired electron of the amide nitrogen.

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The aim of this paper is to bring to view the self-aggregation of C_{60} in this solvent by Surface Enhanced Raman Scattering (SERS) spectroscopy, photoluminescence (PL) and viscosity studies. We like to notice that a few data were reported concerning aggregation of C_{60} investigated by these methods [18-22].

2. Experimental

The solvent, N-methyl-2-pyrrolidinone, and C_{60} powder used in this work were of Merk quality. 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 few minutes and hermetically bottled in quartz cells. The SERS, PL and viscosity measurements on solutions samples were performed at room temperature. Also, for the SERS and PL studies one used C_{60} films 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. The films used for PL measurements were deposited on quartz supports by the evaporation of the solvent.

Viscosities of solutions were determined using a Cannon-Fenske Routine viscometer thermostated in a water bath set at 25 °C.

3. Results and discussion

N-methyl-2-pyrrolidinone acts both as solvent and reactant. Due to the unpaired electrons of the amide nitrogen atom, NMP molecule is particularly reactive against C_{60} . By charge transfer from the solvent molecules, as electron donors, towards fullerene as acceptor are formed complexes, which later on associate in stable aggregates likened to a crystalline network. Fig.1 shows SERS spectra on films of ca. 100 nm thicknesses prepared from solution of C_{60} in NMP, stored in the dark for different time. Gradual modification of the C_{60} spectra relates perturbing contributions coming from the interaction with the metallic substrate, solvent molecules and neighbor fullerenes, when stable clusters are formed. The interaction of C_{60} with the gold substrate is indicated by the band at 342 cm^{-1} whose decrease or disappearance, when the solution is stored for longer time signify the disappearance of C_{60} in its original I_h symmetry. Interaction with the solvent is evidenced by the new band at $\sim 255\text{ cm}^{-1}$, whose variation in the series of SERS spectra from Fig.1 may be associated with two different stages in the self-assembling of C_{60} fullerene. In the beginning, it is a weak shoulder of the band at 270 cm^{-1} , attributed to the $H_g(1)$ mode of $I_h C_{60}$, which increases with the storage time, until it replaces completely the original $H_g(1)$ band. This stage is dominated by the interaction between C_{60} and solvent molecules, when are formed (C_{60} , NMP) charge transfer complexes and small clusters of these. Later by successive association of (C_{60} , NMP) complexes are formed aggregates of greater size with solvent molecules bound within. A shift of this band from 255 at 246 cm^{-1} and strong enhancement of the band at $\sim 94\text{ cm}^{-1}$ which do not belongs to the Raman spectrum of $I_h C_{60}$ [23] characterized this stage. Process resembling with a crystallization, which takes place into saturated solutions.

In this context the appearance of new bands at $1496, 992\text{ cm}^{-1}$ and a broad one around of 758 cm^{-1} has a specific meaning. Imagining the self-assembling of C_{60} in NMP as a slow crystallization process having as discrete unit the early formed (C_{60} , NMP) complex, an aggregate may be described also by a general formula $C_{60}X_y$, typical for a crystalline structures of clathrate type, where X is the solvent molecule bound within [23,24-28]. In this case, by the stronger

interactions with the neighborhood molecules the high I_h C₆₀ symmetry is lowered so the silent and high orders of vibration modes are activated, they becoming observable both in the IR absorption spectra and Raman spectra. This explains also why in the clathrate structures nearly all Raman lines of isolated C₆₀ have their counterparts in the IR spectra, [24]. Fig. 1 shows such a band at 1496 cm⁻¹, which was also, reported in the IR absorption spectra of the C₆₀·4C₆H₆, C₆₀·xCCl₄, C₆₀·C₂HCl₃ clathrates, [25]. The result is an argument that C₆₀ form in NMP aggregates with solvent molecules bound within.

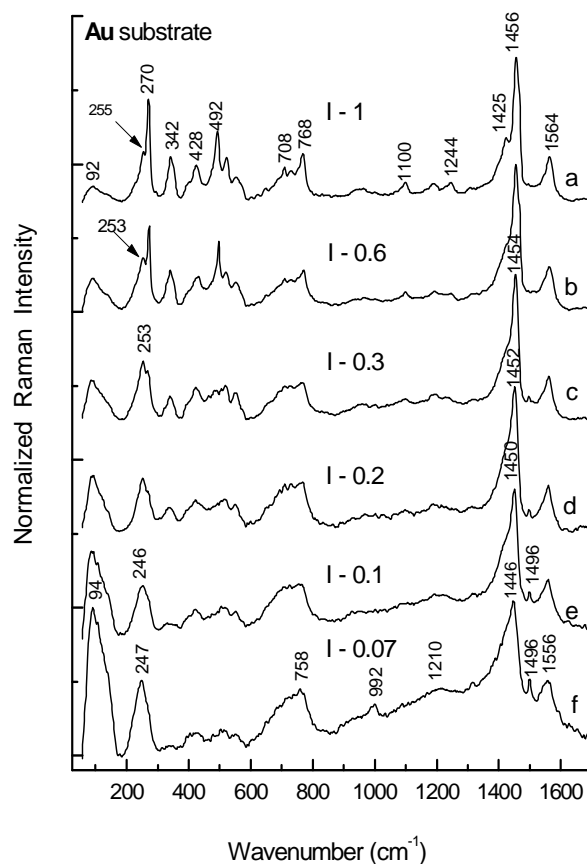


Fig. 1. SERS spectra of C₆₀ in N-methyl-2-pyrrolidinone at $\lambda_{exc}=1064$ nm on films of ca. 110 nm thickness deposited on Au substrate. Spectrum a is for the initial state, i.e., of film prepared from fresh solution, and the spectra b, c, d, e and of films prepared from the solution stored in the dark at ambient temperature for 1, 3, 6, 18 and 34 days, respectively. The concentration of C₆₀ solution was of 0.04 %wt.

In general, into aggregate structure the disparity between the strength of the intramolecular and intermolecular bonds divides the phonon spectrum into intramolecular and intermolecular vibrations, the later being revealed in the low frequency of the Raman spectrum. We think that the band at about 93 cm⁻¹ originates in interball stretching mode by analogy with the Raman lines associated with the covalent bonds between adjacent C₆₀ in dimmers [25-27]. In this case, the downshift at 246 cm⁻¹ of the band formed in the earlier aggregation stage at ~ 246 cm⁻¹ relates many cage bound into chain or network of C₆₀. Again, it is worth to mention that such a band was predicted theoretically as one component for the splitting of the H_g(1) band for C₆₀ dimer [25].

The variation of PL spectra with storage time, for two solutions of different C₆₀ concentration, 2 and 0.5 mg/ml, is presented in Fig. 2A1 and Fig. 2B1, respectively. Curves 1 display the PL spectra recorded on fresh solutions and curves 2 - 8 are the spectra after different

storage time of 2, 6, 13, 43, 445, 647 and 697 days. Both figures reveal an important PL enhancement with some particularities depending on concentration. In the solution of higher concentration the growth of PL is done by the red emission, while the green emission prevails in PL of the solution of lower concentration. Eliminating the contribution of the solvent, by subtracting the spectrum 1 from the each other spectra, one eliminates the data from Fig. 2, A1 and Fig. 2, B1 become more relevant. The difference spectra resulted from (curves 5 – curves 1) and (curves 8 – curves 1) are displayed in a normalized scale in Fig. 2, A2 and Fig. 2, B2, respectively. All these curves were fitted with two Gauss profiles (dotted lines) whose weight in the whole emission depends both of concentration and storage time. One sees clearly that regardless of the concentration of C_{60} , the weight of green emission increases if the solutions are stored longer time. Although the enhancement of PL begins in the red emission and ends in the green band, no connection between their growths was observed.

Supposing that PL emission of (C_{60} , NMP) molecular complexes retains the main characteristics of the new compounds formed, then the two bands existent under curve (5-1) from Fig. 2, A2, at about 1.92 and 2.18 eV, can be considered as the blue and red shifted PL emission of C_{60} fullerene and NMP molecules, respectively. In general, the magnitude of the shift for absorption as well as an emission band depends on the strength of environmental intermolecular interactions. Passing from free C_{60} fullerene as it exists in powder form to solvated C_{60} as in various aromatic solvents, the fluorescence band shifts from 1.68 to 1.77 eV. An additional blue shift of C_{60} emission is expected in NMP, where beside van der Waals forces that acts in commonly used fullerene solvents; other stronger forces related to the donor-acceptor interaction are presented. Consequently, the position of the red emission, at about 1.92 eV is found in agreement with these expectations and the same, the green band at 2.18 eV is the red shifted fluorescence of the solvent from 2.38 eV.

The subsequent aggregation of (C_{60} , NMP) entities in more intricate molecular structures is highlighted in PL curves by an increase of the green band weight (see curve (8-1), Fig. 2, A2). Considering the green component, as the signature of perturbed NMP molecules, the enhancement of this is explainable if in the new structure besides (C_{60} , NMP) entities are bound within more and more solvent molecules. By analogy with some crystallization processes from aqueous solutions these additional solvent molecules become fixed in the aggregated structure as water molecules into crystalline structure. For C_{60} fullerenes a clathrate structure [28] is the most appropriate.

Careful analysis of the curves (8-1) from Fig. 2, A2 and Fig. 2, B2 reveals that in the case of less concentrated solution the green band occurs around 2.30 eV, closer to the fluorescent band of solvent molecules. Considering the red shift as a measure of the perturbation degree of the incorporated NMP molecules, we must accept that the aggregates formed at longer storage time in diluted solutions are not identical with those formed in concentrated solutions where the green band is found at about 2.22 eV.

There are two ways to explain this result. One by analogy with the crystallization from liquid phase: in solution of higher concentration a rapid crystallization occurs, which leads to many and less perfect crystallites of smaller size, while in the less concentrated solution the crystallization develops slowly forming larger and ordered three-dimensional crystalline structures. Another way to explain proceeds from the hypothesis that the dipole moment of (C_{60} , NMP) entities formed in concentrated and in diluted solution, respectively is not the same. Idea is somehow sustained by recent electrooptical measurements [18], which put in evidence the generation, only in diluted solutions, of polar asymmetric C_{60} complexes with NMP molecules. In this scenario, a stronger dipolar character favours the insertion of more NMP molecules, which are also polar species, into the aggregated structures.

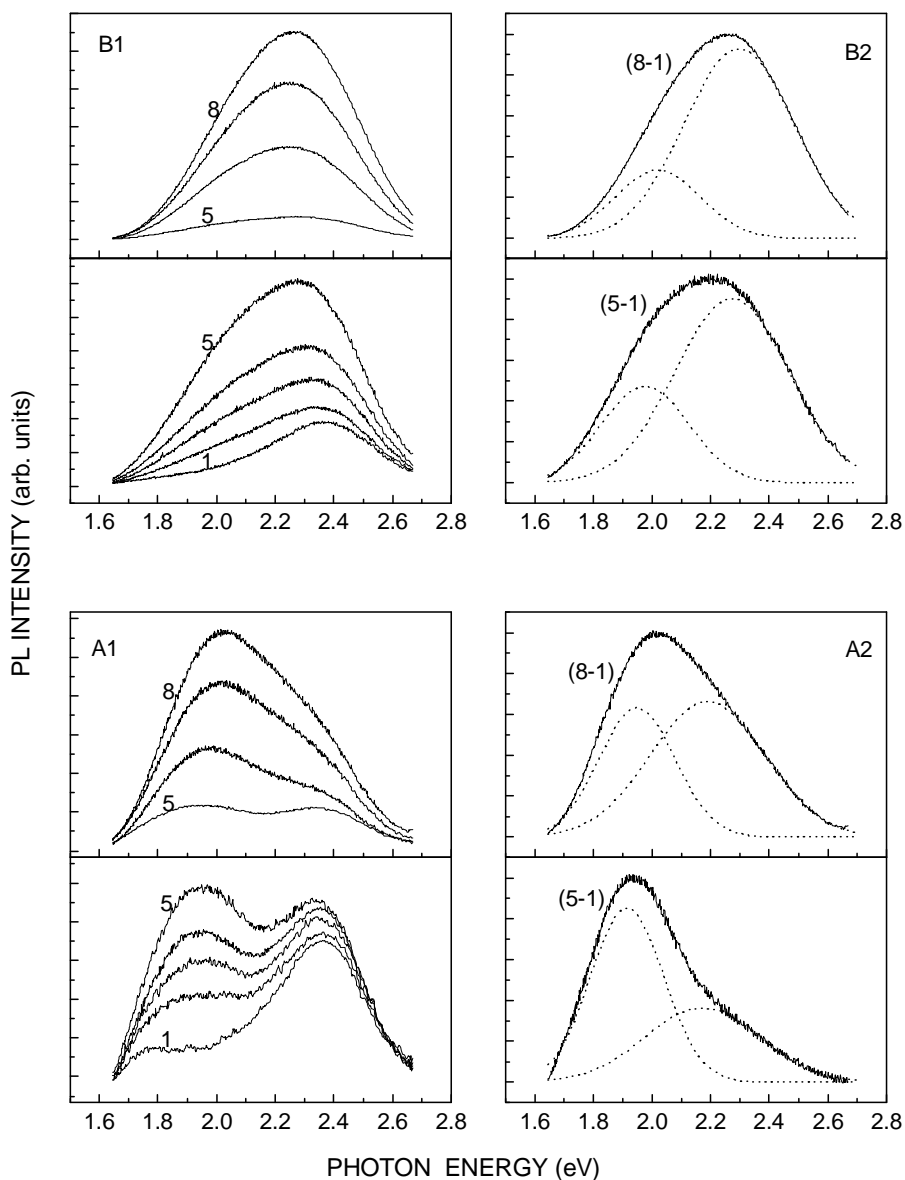


Fig. 2. Variation of PL spectra A1 and B1 with storage times for two C_{60} solutions in NMP of 2 and 0.5 mg/ml concentration, respectively. Curves 1 correspond to fresh prepared solutions. Curves 2 - 8 show PL emission after a storage time of 2, 6, 13, 43, 445, 647 and 697 days. Difference spectra (5-1) and (8-1) in a normalized scale are presented in A2 and B2, respectively. With dotted line is shown the result of spectra fit with two Gauss functions.

A plausible explanation for genesis of such different (C_{60} , NMP) molecular complexes could be found out in the particularities of intermolecular interaction between C_{60} fullerene and NMP. It is known that C_{60} is a mild electron acceptor [29, 30]. On the other hand, a presumable internal conjugation of lone pair electrons belonging to amine nitrogen, with the electrons of carbonyl group, (p - π conjugation), does from the NMP molecule a weaker donor of electrons. In these circumstances, more solvent molecules in the proximity of C_{60} fullerene, as in diluted solutions, advantages evidently a charge transfer process.

Similar results were obtained on thin films prepared by the solvent evaporation. Fig. 3

shows a photoluminescence covering the same spectral range whose maximum shifts towards higher energy with decreasing of the fullerene concentration.

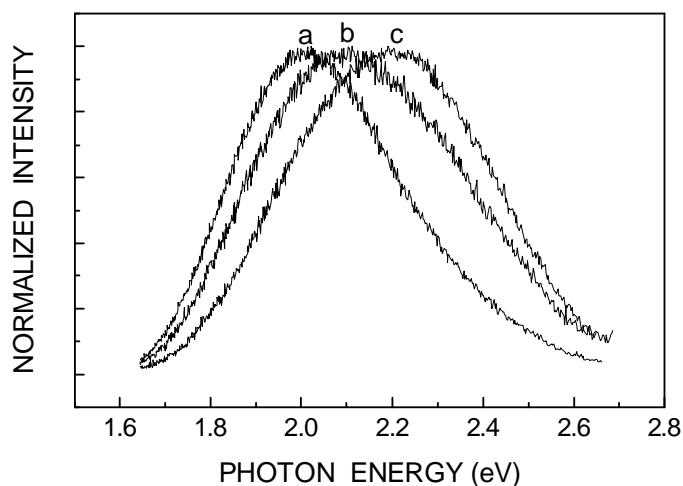


Fig. 3. Normalized PL spectra of thin films prepared from three aged C_{60} solutions in NMP with fullerene content of 2, 1 and 0.5 mg/ml, curves a, b and c, respectively.

The achievement of an intense charge transfer process between fullerene and NMP is also observed by viscosity measurement carry out on diluted C_{60} solutions (Fig. 4). As expected, the variation of viscosity depends on the fullerene concentration. No dramatic changes in the specific viscosity were observed in the solution of high fullerene concentration. Contrary, in the solution of lower concentration, the increase of viscosity was faster in the first week of storage and slower hereinafter. Such a result sustains the presumption that the aggregation of C_{60} in NMP evolves in two stages: initially by a charge-transfer process are formed molecular complexes which latter on associate slowly in stable and larger aggregates.

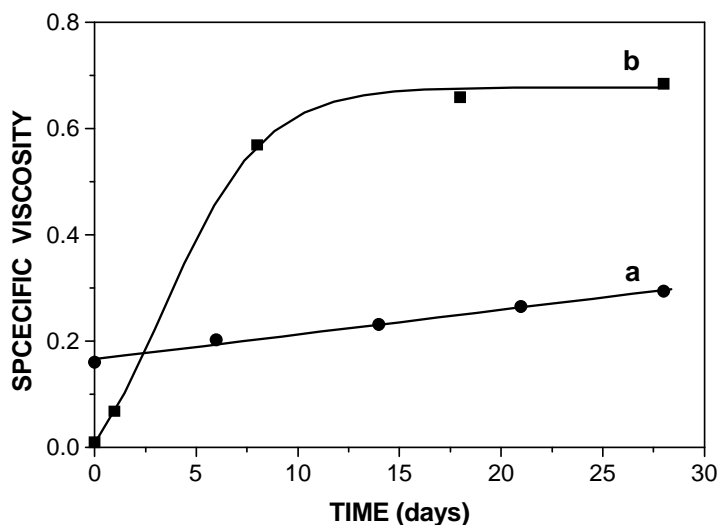


Fig. 4. The specific viscosity as a function of storage time at 25 °C for two C_{60} solutions in NMP of 1 and 0.5 mg/ml concentration, curves a and b, respectively.

4. Conclusions

We have studied by SERS spectroscopy, photoluminescence and viscosity the aggregates of C₆₀ formed in N-methyl-2-pyrrolidinone. Self-assembling of C₆₀ in such a nucleophilic solvent is driven by forces originating in charge transfer from the solvent molecules as electron donors towards fullerene as acceptors.

Aggregation of C₆₀ in NMP develops in two stages: in the beginning are formed quickly the charge-transfer molecular complexes, which on associate slowly in stable aggregates. For this stage, the main indicative in the Raman spectrum is the decreasing and disappearance of the Raman bands associated to the radial vibration modes and a new band at ~255 cm⁻¹ relating the interaction between C₆₀ and NMP molecules. In the second stage this band shifts at ~246 cm⁻¹ and together with a new band at ~94 cm⁻¹ associated to the interball vibration mode become the strongest Raman bands in the low frequencies range. The two positions at 246 and 255 cm⁻¹ of supplementary band raised by the aggregation and interaction with NMP solvent, coincide with the predicted component resulted from the splitting of the H_g(1) band of the I_h C₆₀ into three component at 275, 254 and 242 cm⁻¹ in the C₆₀ dimmer. Whole aggregation process has many similarities with a crystallization that leads to ordered structures like a crystalline lattice.

Intermolecular interactions between C₆₀ fullerene and NMP solvent molecules are revealed in PL spectra by an emission whose intensity increases gradually with the storage time of solutions. Two emission bands, red and green, situated in the interval 1.92-2.00 eV and 2.18-2.30 eV, respectively were identified. Their weight in the whole PL emission depends on the concentration of C₆₀ and on the age of the solutions. Red emission is the dominant component in more concentrated solutions. The green emission prevails in diluted solutions and increases at longer storage time for all used concentrations. PL data show that the two PL bands are the result of two successive processes. The first one, faster, relates a charge transfer between C₆₀ fullerene as acceptor and NMP molecules as donor forming (C₆₀, NMP) molecular complexes, which preserve in the greatest part the emission characteristics of the original molecules. The second process implies a slow aggregation of previously formed (C₆₀, NMP) molecular complexes. In this step, the process goes on with the active participation of solvent molecules, which end up being incorporated in the structure of newly born aggregates.

The viscosity results put in evidence that the solution of lower concentrations favored the formation of C₆₀ aggregates of greater size.

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