



# LONG TERM STUDY OF FULLERENE C<sub>60</sub><sup>++</sup> RADICAL CATION BY ELECTRON SPIN RESONANCE (ESR)

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The dissolution of fullerene C<sub>60</sub> in oleum (fuming sulphuric acid 20 % free SO<sub>3</sub>) was followed simultaneously with ESR (Electron Spin Resonance) and NIR (Near Infrared Spectroscopy). It is shown that the intensity of the ESR signal associated to the formation of C<sub>60</sub><sup>++</sup> radical cation (C<sub>60</sub><sup>++</sup>) follows the same kinetics as the NIR absorption band at about 938 nm. Thus, the band at about 938 nm represents the optical counterpart of the ESR signal of C<sub>60</sub><sup>++</sup>. After the formation of C<sub>60</sub><sup>++</sup>, the evolution of the ESR spectrum and its optical counterpart in the NIR suggest the formation of other fullerene oxidation products as well. These products were recovered from the oleum solution and analyzed with FTIR and found to be fullerol (hydroxylated derivative of fullerene). The work-up of the oleum solution led to the desulfonation of the substrate. The ESR signal of C<sub>60</sub><sup>++</sup> in oleum was followed for two weeks. Even after so long time, the ESR signal appeared strong and clear although under slow decay. Thus, the oxidation species of C<sub>60</sub><sup>++</sup> (polycations, dimers and oligomers of C<sub>60</sub>, sulfonated and sulfated derivatives) are persistent radicals in oleum.

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## Introduction

Fullerene C<sub>60</sub> is widespread in the Universe<sup>1</sup> as demonstrated by recent discoveries essentially based on the detection of infrared emission bands of this molecule.<sup>2-4</sup> The detection of fullerene in young planetary nebulae and in other astrophysical environments as well as the quantification of its relative abundance in space was made possible thanks to the laboratory studies made on the infrared spectrum of C<sub>60</sub>, on its derivatives and on the determination of the molar extinction coefficients and integrated molar absorptivities.<sup>6-13</sup>

Although C<sub>60</sub> has been detected in the infrared in space, its detection in the ultraviolet and in the visible part of the spectrum has not yet been achieved for a number of reasons, including the fact that, especially in the ultraviolet, there are a number of different “carriers” emitting in that spectral region, covering the possible “spectral signature” of C<sub>60</sub>. On the other hand, it is known that C<sub>60</sub> in the interstellar medium should be ionized into its radical cation form: C<sub>60</sub><sup>++</sup>.<sup>1,14</sup> The ionization mechanism involves the extraction of one electron from the C<sub>60</sub> molecule by the action of cosmic rays and it is favored by the relatively low first ionization potential of C<sub>60</sub> (E<sub>i</sub>=7.61 eV). The electronic absorption (and emission) spectrum of C<sub>60</sub><sup>++</sup> is characterized by the presence of electronic transitions in the near infrared, a spectral region relatively less crowded by the interference of other molecules than in the ultraviolet. In a previous work, we have determined the molar extinction coefficient of the C<sub>60</sub><sup>++</sup>.<sup>15</sup> The radical cation bands are characterized by a molar extinction coefficient ε<sub>823</sub> = 7500 L cm<sup>-1</sup> mol<sup>-1</sup> and ε<sub>943</sub> = 4570 L cm<sup>-1</sup> mol<sup>-1</sup>.<sup>15</sup>

The most typical approach for the synthesis of C<sub>60</sub><sup>++</sup> involves the high energy irradiation of neutral C<sub>60</sub> trapped in frozen matrix of helium or neon.<sup>16-19</sup> The advantage of this technique regards the minimization of the so-called “matrix effect” which involves a band shift due to the interaction of the guest molecule with the host matrix. Helium and neon are completely inert matrices and the interaction with the guest radical cation is considered negligible. On the other hand, another approach used to generate radical cations in laboratory involves the use of a superacid medium.<sup>20</sup> The most popular superacid is fuming sulfuric acid (oleum) as solvent and oxidizing medium.<sup>21-30</sup> Alternatively triflic acid and an oxidant<sup>22</sup> or other sophisticated superacids were used successfully.<sup>31,32</sup>

Although the use of superacids as medium for the generation of the radical cations is more practical, there is the problem that the strong interaction of the radical cation with the superacid medium may cause important band shift of the radical cation band transitions in the near infrared and also a limited lifetime of the in situ generated radical cation specie.<sup>15,22,23,31</sup> However, as discussed by us in a earlier paper<sup>15</sup> and as summarized in a review,<sup>31</sup> at least for the C<sub>60</sub><sup>++</sup> the band shift in the optical spectra by passing from He or Ne matrix to a superacid medium is really small and could be considered as negligible.

The optimal approach for the study of the radical cation species is always the combination of the optical spectroscopy with the electronic paramagnetic resonance (EPR) or electron spin resonance (ESR) spectroscopy. The confirmation of the formation of the radical cation derives exclusively from the ESR signal to which it is associated the optical counterpart in the visible or in the near infrared. Indeed, the first work on C<sub>60</sub><sup>++</sup> in oleum was made with ESR spectroscopy.<sup>21</sup> Only later, the C<sub>60</sub><sup>++</sup> in oleum was analyzed by optical spectroscopy.<sup>22</sup> However, also in recent works quite rarely the ESR spectroscopy was applied to C<sub>60</sub><sup>++</sup> simultaneously with the near infrared (NIR) spectroscopy.<sup>15,23,30</sup>

The present paper is dedicated to the simultaneous investigation of  $C_{60}^{++}$  in oleum both with ESR and NIR. The investigation is not limited to the early minutes of interaction of  $C_{60}$  with oleum but it was prolonged for several days after the fullerene dissolution and oxidation with the purpose to verify the stability of  $C_{60}^{++}$  in oleum and eventually to detect its dimerization reaction<sup>25-29</sup> as well as further reactions with the host matrix which involve sulfonation and sulfation reactions.

## Experimental

### Materials and Equipment

$C_{60}$  was obtained from Aldrich (USA) and was 99.5% pure. Oleum (fuming sulphuric acid) 20 % free  $SO_3$  and was obtained from Sigma-Aldrich (Germany).

The near infrared spectra were recorded on Nicolet 6700 FT-NIR spectrometer from Thermo Scientific using a  $CaF_2$  beam splitter. The oleum solution of  $C_{60}$  was analyzed in a conventional quartz cuvette having 5 mm path length and sealed with a Teflon stopper.

The mid-FT-IR spectra were recorded on KBr pellets Nicolet 6700 FT-IR spectrometer from Thermo Scientific using a KBr beamsplitter.

The ESR spectra were obtained on a X-band spectrometer from Active Spectrum model Micro-ESR using 2 mm internal diameter quartz capillaries. Each spectrum recorded was the average of 20 scans.

### Preparation of the $C_{60}$ solution in oleum

Fullerene  $C_{60}$  (8.8 mg) was quickly shaken with oleum (7 g) in a flask with stopcock. After 1 min shaking the heterogeneous solution was pipetted into the ESR capillary tube and the first spectra recorded immediately after the necessary tuning operations of the spectrometer. Simultaneously, the same  $C_{60}$  solution in oleum was also studied with the FT-IR spectrometer in the near infrared spectral region.

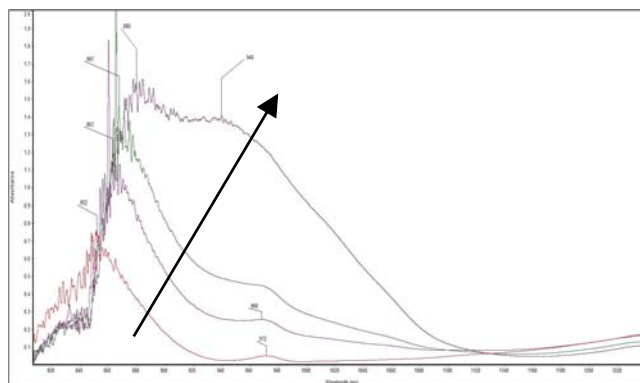
### Recovery of $C_{60}$ oxidation products from oleum

After 15 days of preparation, the above mentioned solution of  $C_{60}$  in oleum was poured into 100 ml of distilled water, stirred and left to settle. A brown-orange precipitate was deposited at the bottom of the flask. The water was decanted and new distilled water was added, the mixture was stirred and decanted until neutrality was reached as measured with the pH test paper. Water was decanted again and the residual water was evaporated in a water bath at 80 °C until dryness. About 10 mg of brown-orange product was recovered and studied with FT-IR spectroscopy.

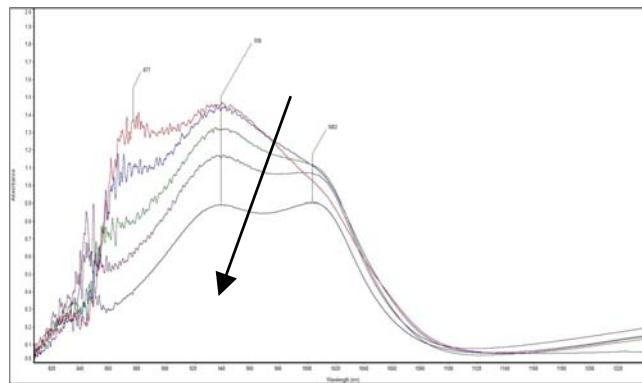
## Results and Discussion

### Near Infrared (NIR) spectra of $C_{60}^{++}$

The NIR spectra of  $C_{60}^{++}$  were already shown and discussed in earlier works.<sup>15,22,23</sup> Fig. 1 and 2 show the NIR spectra of  $C_{60}^{++}$  as recorded with the FT-NIR. The spectra are substantially analogous to those recorded in a conventional spectrophotometer. The novelty in the present case is the spectral range covered from 800 to 2000 nm while in the previous works the spectral range analyzed was from 190 to 1100 nm.<sup>15,22,23</sup> However, no additional features were detected above 1100 nm attributable to  $C_{60}^{++}$ .



**Figure 1.** FT-NIR spectrum of  $C_{60}^{++}$  in oleum. The spectra were recorded in the first hour after mixing and are characterized by a steady growth in intensity as shown by the arrow pointing upward.



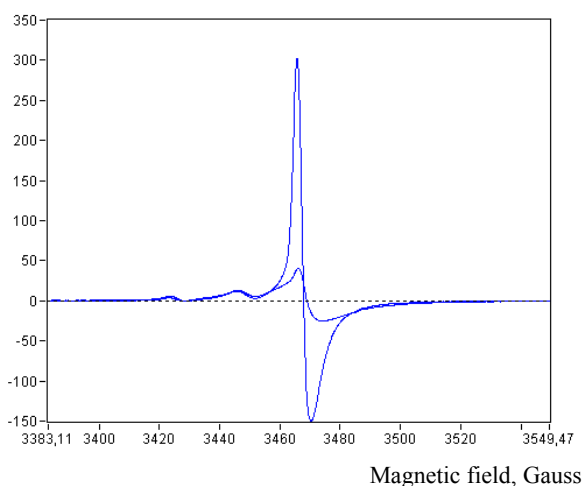
**Figure 2.** FT-NIR spectrum of  $C_{60}^{++}$  in oleum. The spectral evolution till 5 h after mixing show now a steady decrease in intensity as indicated by the arrow pointing downward. However, after 5 h the two bands at 938 nm and 1003 nm result stable for very long time.

Fig.1 reports a series of spectra recorded in the first hour of mixing. It shows a steady growth in intensity of the absorption bands. There is the steady growth of the absorption band at 852 nm which is shifted at 867 nm and then 880 nm with time. Another weak feature can be observed at about 970 nm. The mixture is not showing a stable spectral pattern. In fact, between the first and the fifth hour after mixing there are further changes as shown in Fig.2. This time the initially fast growing band at 880 nm is disappeared.

The broad band at 970 nm is now decreasing in intensity and can be found at about 938 nm. There is another band at about 1003 nm which is developed at later stages reaching approximately the same intensity of the band at 938 nm. The overall spectral changes are completely in line with earlier results.<sup>15,22,23</sup>

### Electron Spin Resonance (ESR) spectra of $C_{60}^{+}$

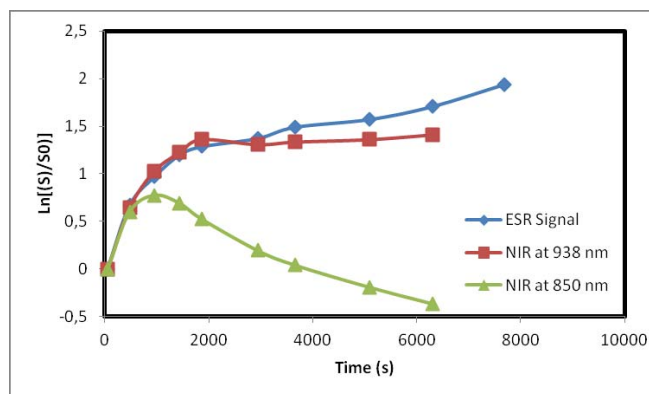
As soon as mixed with oleum  $C_{60}$  gradually dissolves into the guest matrix giving a green solution. The ESR signal of  $C_{60}^{+}$  can be recorded immediately after mixing as shown in Fig. 3 and the signal grows in intensity for at least the first hour after mixing. Fig. 4 shows the kinetics of growth of the peak-to-peak amplitude of the ESR signal in comparison to the kinetics of optical counterpart recorded in the NIR at about 938 nm and at about 850 nm. In Fig. 4, it is evident that the kinetics of the absorption band at about 938 nm overlaps with the ESR signal, while the other band at about 850 nm is following another destiny. Therefore, the absorption band at about 938 nm must be necessarily assigned to the  $C_{60}^{+}$  while the other band at about 850 nm is instead due to charge-transfer interactions with the solvent as it was previously supposed.<sup>15,22,23</sup>



**Figure 3.** ESR spectra of  $C_{60}$  in oleum. The smaller signal was taken 1 min after mixing and the largest signal after 130 min

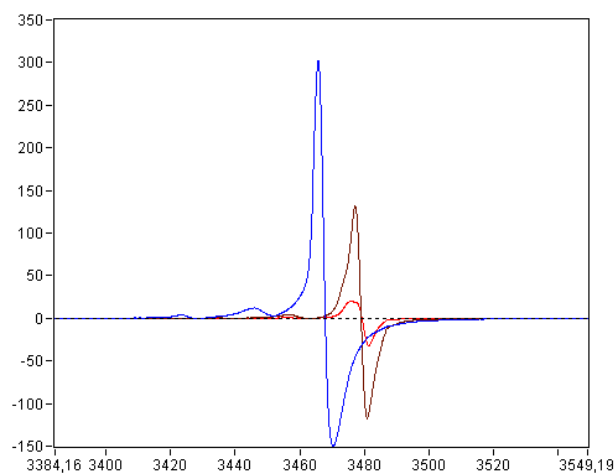
Fig. 4 provides for the first time the unambiguous assignment of the NIR band at about 938 nm to  $C_{60}^{+}$  and the attribution of the other band at about 850 nm to initial charge-transfer interaction phenomena of  $C_{60}$  with the superacid at the beginning of the dissolution. With this interpretation it can be affirmed that at room temperature the  $C_{60}$  dissolution in oleum is completed in about 1h.

In Fig. 4 the optical absorption data in the NIR were plotted as  $\ln[(Abs)/(Abs)_0]$  against time, where (Abs) is the absorption at a given wavelength taken at any time and  $(Abs)_0$  is the absorption at the same wavelength taken at the beginning of the experiment. Similarly, in Fig. 4 the peak-to-peak amplitude of the ESR signal was plotted as  $\ln[(ESR)/(ESR)_0]$  against time, where (ESR) is the peak-to-peak amplitude of the ESR signal taken at any time and  $(ESR)_0$  is the peak-to-peak amplitude of the ESR signal taken at the beginning of the experiment.



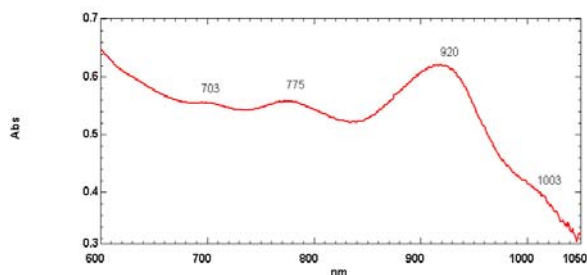
**Figure 4.** Kinetics of the ESR signal growth in the first two hours after mixing (blue diamonds) and the kinetics of the optical counterpart spectra measured in the NIR. It is evident that the kinetics of the band at about 938 nm (red squares) is practically the same as that of the ESR signal, while the other band at about 850 nm (green triangles) is following another destiny.

The first ESR spectrum of  $C_{60}^{+}$  taken and reported in Fig. 3 shows a  $g$  value of 2.08632 while the latest spectrum recorded after 2 h shows a  $g$  value of 1.90344. The main line width of the first ESR spectrum of Fig.3 is 7.8 G and it becomes narrower 4.7 G after 2 h. The line width of the other smaller signal in the left of the main signal are respectively 5.1 and 6.0 G in the first ESR spectrum recorded. The zero-field parameters  $|D|$  and  $|D/2|$  as defined by Tumanskii et al.<sup>27</sup> were found at 45.24 and 23.37 G respectively. After 2h the  $|D|$  and  $|D/2|$  parameters were still found at 44.9 and 22.2 G. The ESR spectra of  $C_{60}$  in oleum were interpreted in terms of radical cation formation followed by further oxidation which leads to the trication and pentacation.<sup>21</sup> A series of deeper investigations has instead suggested that the radical cation of  $C_{60}$  tends to dimerize and oligomerize in oleum leading to the formation of  $C_{120}O^+$  and  $C_{120}O^{2+}$ .<sup>25-29</sup> However, such dimerization/oligomerization reaction occurs when large amounts of  $C_{60}$  are dissolved in oleum. Solodovnikov showed that the line width of  $C_{60}^{+}$  when generated in a mixture of toluene/sulphuric acid is about 7 G, was very close to the 7.8 G line width value found in our earlier spectrum (Fig. 3) recorded immediately after the initial dissolution of  $C_{60}$  in oleum.<sup>25,27</sup>



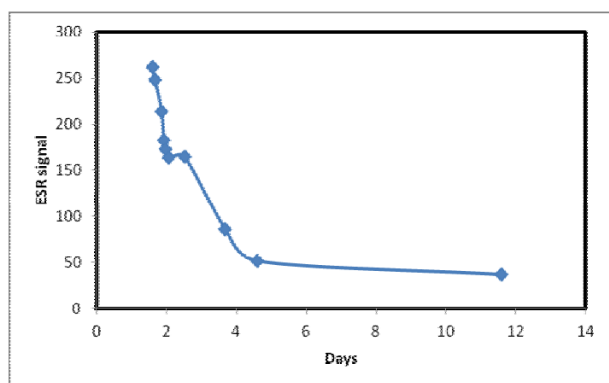
**Figure 5.** ESR spectra of  $C_{60}$  in oleum. The largest signal is the same as Fig. 3 taken after 130 min. The other two signals were taken respectively after 40 h and 110 h.

Till now, nobody has followed the ESR of  $C_{60}$  solution in oleum sealed in a capillary quartz tube for a long time. After the initial green-grey color, the  $C_{60}$  solution in oleum turns gradually into orange-brown. Fig. 5 shows the ESR spectra of such solution at 40 and 110 h after preparation. Surprisingly after 40 h and beyond, the ESR spectra appear shifted about -11.3 G from the original position. The g factor is now 2.09184 and the main line width is now 3.76 G, thus the signal is narrower than that of the “fresh” sample. The changes of the ESR parameters may suggest that we are dealing with other reaction products. The optical counterpart of the long term experiment of  $C_{60}$  in oleum is shown in Fig. 6. The NIR spectrum after 5 days from preparation still shows the absorption bands attributed to  $C_{60}^{++}$  at 920 and 1003 nm. However two new absorption bands at 703 and 775 nm can be observed in Fig. 6 and assigned to other species than  $C_{60}^{++}$ .



**Figure 6.** NIR spectrum of  $C_{60}$  in oleum after 5 days from preparation.

The long term evolution and decay of the ESR signal (peak-to-peak amplitude) can be followed in Fig. 7. Even after two weeks from the beginning of the experiment the ESR signal is still clearly detected (see also Fig. 5). Fig. 7 suggests that the ESR signal (although weak) could be detected even after 1 month after the preparation.

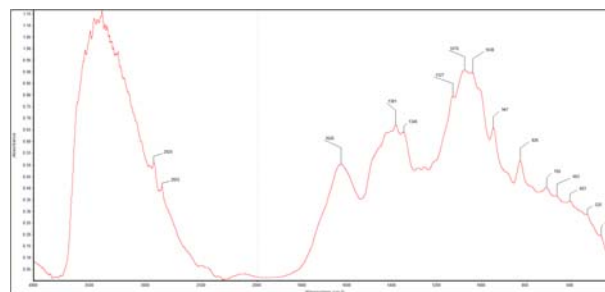


**Figure 7.** Long term evolution of the ESR signal of  $C_{60}$  in oleum.

#### FT-IR spectroscopy of the $C_{60}$ oxidation product recovered from oleum

When the  $C_{60}$  solution in oleum is poured into an excess of water a brown-orange insoluble precipitate is obtained.<sup>24,28,29,35</sup> It is necessary to wash carefully with water to neutrality the precipitate to remove the contamination of residual sulfuric acid.<sup>28,29</sup> The resulting FT-IR spectrum of our sample is shown in Fig. 8 and it is partly similar to that

shown by other authors.<sup>28</sup> However, the spectrum of Fig. 8 resembles that of fullerol which is characterized by three main bands at 1595, 1385 and 1085  $cm^{-1}$ .<sup>35</sup> Indeed, the spectrum of Fig. 8 shows three main broad infrared bands at 1626, 1381, 1076  $cm^{-1}$ . This implies that sulfonation/sulfation of  $C_{60}$  in oleum was a minor reaction.



**Figure 8.** FTIR spectrum of  $C_{60}$  oxidation product recovered from oleum solution

However, Taylor has proposed that the sulfonation followed by hydrolysis leads to fullerol with an almost complete removal of the  $SO_3H$  groups.<sup>35</sup> The presence of oxygenated sulfur functionalities in the infrared spectrum can be deduced from the S-O stretching in the asymmetric ( $1320-1390\text{ cm}^{-1}$ ) and in the symmetric mode ( $1150-1200\text{ cm}^{-1}$ ).<sup>36</sup> Fig. 8 is lacking completely the asymmetric stretching mode of S-O group ruling out any important presence of the oxygenated sulfur functionalities. Thus, the precipitate recovered from  $C_{60}$  oleum solution is indeed fullerol. The eventual dimeric/oligomeric structure of this product, as suggested by other authors,<sup>28,29</sup> cannot be established on the sole basis of the infrared spectra.

#### Conclusions

The most important result of the present work is the discovery that the peak-to-peak amplitude of the ESR signal associated to  $C_{60}^{++}$  formed in oleum, grows in intensity with the same kinetic law followed by the optical NIR counterpart band at about 938 nm as shown in Fig. 4. Based on these results it is obvious to associate the 938 nm band with the radical cation of  $C_{60}$  species. The other band at about 850 nm observed in the NIR spectrum at the beginning of the dissolution of  $C_{60}$  in oleum is correctly assignable to a charge-transfer interaction of  $C_{60}$  with oleum in the early stages of its dissolution as already stated previously.<sup>15,22,23</sup>

The formation of  $C_{60}^{++}$  in the first hours of dissolution of  $C_{60}$  in oleum is also confirmed by the line width of the ESR spectrum which corresponds to that already reported in literature for this species.<sup>25,27</sup>

The long term interaction (days) of  $C_{60}^{++}$  with oleum causes a shift of the ESR spectrum and changes in the line widths of the spectrum. It is evident that this is due to further reactions of  $C_{60}^{++}$  with oleum which can lead to the formation of polycations<sup>21</sup> or to the formation of oligomers of  $C_{60}$  for example of the type  $C_{120}O^+/C_{120}O^{2+}$ .<sup>25-29</sup> This



second hypothesis is corroborated by a quite extensive body of works but does not exclude also the first hypothesis. C<sub>60</sub><sup>++</sup> or its further oxidation product may undergo in the long term sulfonation and sulfation reactions.<sup>33-35</sup> This fact is completely reasonable and expected. Less obvious is the absence of evidences of the S-O symmetric stretching band in the FT-IR spectrum of the C<sub>60</sub> oxidation product recovered from the oleum solution. According to Taylor,<sup>35</sup> the sulfur-bearing functionalities are released by hydrolysis during the work-up leading to the formation of a fullerol as indeed is suggested by the FT-IR spectrum of Fig. 8.

Even after 2 weeks of the preparation of the C<sub>60</sub> solution in oleum it is possible to detect a strong and clear ESR signal from the solution. This means that the species derived from C<sub>60</sub><sup>++</sup> further oxidation (polycations, oligomers and sulfonated/sulfated derivatives) are then quite stable in oleum. The NIR spectrum after 5 days from preparation still displays the absorption band at 920 nm associable to the C<sub>60</sub><sup>++</sup>. This band is however accompanied by other bands which may account for the presence of other species (see Fig. 6).<sup>1</sup>

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