



# ON THE MOLAR EXTINCTION COEFFICIENTS OF THE ELECTRONIC ABSORPTION SPECTRA OF $C_{60}$ AND $C_{70}$ FULLERENES RADICAL CATION

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Fullerene  $C_{60}$  and  $C_{70}$  were discovered in 2010 by means of infrared spectroscopy in a series of astrophysical objects like for example planetary and protoplanetary nebulae and reflection nebulae. These discoveries suggest that  $C_{60}$  and  $C_{70}$  must be widespread in the interstellar medium and may contribute as neutral species or as radical cation ( $C_{60}^{+}$  and  $C_{70}^{+}$ ) to the DIBs, the Diffuse Interstellar Bands which are attributed to the electronic transitions of molecules and radicals. In this paper are reported the electronic absorption spectra of both  $C_{60}$  and  $C_{70}$  and of their radical cations  $C_{60}^{+}$  and  $C_{70}^{+}$  together with the molar extinction coefficients of all the main absorption bands. All these experimental data are key tools for the qualitative and quantitative search and recognition of these molecules and radicals in space using electronic transitions rather than infrared transition. Furthermore, the electronic absorption bands and molar extinction coefficients of hydrogenated and perdeuterated fullerenes (known as fullerenes) and higher fullerenes are reported.

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Since fullerenes  $C_{60}$  and  $C_{70}$  are present in space not only around certain astrophysical objects but also in the interstellar medium, they can undergo ionization in the harsh interstellar environment and may be detected as ions rather than as neutral species. Indeed, the first claim of fullerene detection in space involved the  $C_{60}^{+}$  rather than neutral species.<sup>1</sup>

The electronic absorption spectra of  $C_{60}$  and  $C_{70}$  fullerenes in the ultraviolet and in the visible, the analogous emission spectra and the spectra of the radical cation of these species are characterized by large cross section (i.e. molar extinction coefficients) which exceed by orders of magnitude the molar extinction coefficients in the infrared. Thus, if fullerenes were firmly detected in space through their infrared bands and their relative abundance was estimated through the molar extinction coefficients and molar absorptivity measured in laboratory, they must be detectable in space also in the spectral range comprised between 190 and 1500 nm where we know that the space is rich of a number of yet unassigned electronic transitions belonging to molecules and radicals (the so-called DIBs = Diffuse Interstellar Bands). Consequently the present work other than being a summary of the absorption bands of  $C_{60}$  and  $C_{70}$  in the ultraviolet and visible reports for the first time the molar extinction coefficients of the radical cation spectra of  $C_{60}^{+}$  and  $C_{70}^{+}$  to permit not only the identification of these species in space but also the determination of their relative abundance.

## INTRODUCTION

Some years ago, Ehrenfreund and Foing<sup>1</sup> assigned tentatively to fullerene radical cation [ $C_{60}^{+}$ ] some spectral features observed in the diffuse interstellar bands. Because of the lack of other experimental evidences (for example the infrared counterpart) the existence of fullerene in space remained uncertain until 2010 when Cami et al.<sup>2</sup> detected the infrared spectral signature of neutral  $C_{60}$  around a young planetary nebula called Tc1. This discovery was followed by a series of confirmations so that now it is known that fullerenes  $C_{60}$  and  $C_{70}$  are widespread in the Universe not only in certain planetary nebulae but also in protoplanetary nebulae, certain carbon-rich stars including also certain R-Coronae Borealis stars type and even in the interstellar medium, in certain reflection nebulae.<sup>3-6</sup>

The infrared spectra of a series of reference fullerenes and fullerenes have been recorded in the laboratory by Iglesias-Groth et al.<sup>7,8</sup> together with the relative molar absorptivity and molar extinction coefficient of the infrared bands. This recent laboratory spectroscopy of  $C_{60}$  and  $C_{70}$  fullerenes has permitted an accurate determination of the fullerene abundances in space, e.g. an abundance of about 0.35% in certain planetary nebulae was determined.<sup>3,4</sup> In addition, because the reference spectra of hydrogenated fullerenes (fullerenes) are now available, a search for these molecular species can be made in space, and their possible detection in astrophysical environments may be only a matter of time and luck.

## EXPERIMENTAL

### Materials and Equipment

Fullerenes  $C_{60}$  and  $C_{70}$  were high purity grades (99,95% and 99,0+%, respectively) from MTR Ltd. (USA).

Oleum (fuming sulphuric acid) with 30% free  $SO_3$  was from Merck (Germany) while another oleum sample used was 20% free  $SO_3$  and was obtained from Sigma-Aldrich (Germany).

The electronic absorption spectra of the radical cations were recorded on a Shimadzu UV2405 spectrometer in the range of 190–1100 nm (6.53–1.13 eV). Optical grade quartz UV cuvettes were used for recording the spectra.

### Generation of the fullerene radical cation and determination of the molar extinction coefficient

Warning! Oleum is an extremely corrosive and powerful oxidizing agent. The fumes released by oleum must not be breathed. Wear suitable protective gloves and goggles and always work under an appropriate fume hood.

After a baseline correction (oleum vs. oleum), the spectra of the fullerene radical cations were recorded by dissolving in oleum (50 ml) about 1–10 mg of the accurately weighed fullerene under study. To ensure a rapid dissolution, the 50 ml flask containing oleum and solid of C<sub>60</sub> or C<sub>70</sub> was sonicated for maximum 5 min. Since the amount of fullerene was extremely small in comparison to the volume of the solution, the dissolution was complete in 5 min yielding a green solution in the case of C<sub>60</sub><sup>+</sup> and a brown-reddish solution in the case of C<sub>70</sub><sup>+</sup>. The spectra were recorded immediately after the dissolution and in the case of C<sub>60</sub><sup>+</sup> the evolution of the band at 823 nm was followed together with that at about 943 nm. The spectrum of the C<sub>70</sub><sup>+</sup> appears more stable in oleum than that of C<sub>60</sub><sup>+</sup>.

The molar extinction coefficient  $\epsilon$  was determined through the well-known Lambert-Beer relationship:

$$\epsilon = Ab^{-1}c^{-1} \quad (1)$$

where  $A$  is the absorbance measured at a given wavelength,  $b$  is the path length of the quartz cell used for the measurement (1 cm) and  $c$  is the concentration of C<sub>60</sub> or C<sub>70</sub> dissolved in oleum and expressed in mol L<sup>-1</sup>.

## RESULTS AND DISCUSSION

### The electronic absorption spectrum of C<sub>60</sub> fullerene

Fullerene C<sub>60</sub> due to its 30 weakly conjugated double bonds displays a very interesting, complex and characteristic absorption spectrum in the ultraviolet. The spectrum is shown in Fig. 1. C<sub>60</sub> shows two intense bands at 209 and 255 nm, respectively, with a molar extinction coefficient  $\epsilon$  of 135000 and 175000 L cm<sup>-1</sup> mol<sup>-1</sup>. The other absorption band of C<sub>60</sub> appearing in the ultraviolet is located at 327 nm ( $\epsilon = 51000$  L cm<sup>-1</sup> mol<sup>-1</sup>). In the visible the spectrum of C<sub>60</sub> is dominated by a band at 404 nm (see Fig. 2) and by a broad and relatively weak groups of band between 440 and 670 nm with subfeatures at 500, 530, 570, 600 and 628 nm.

The electronic absorption spectra of C<sub>60</sub> and C<sub>70</sub> were studied by several authors<sup>9–13</sup> and the relative molar extinction coefficients were determined in the mentioned earlier works. In view for the search of fullerenes in the gas

phase in the interstellar medium there are some works dealing with the solvent effect on fullerene spectra.<sup>10–13</sup> Fullerenes have a very low volatility and consequently it is necessary to record their electronic absorption spectra in liquid phase dissolved in solvents.

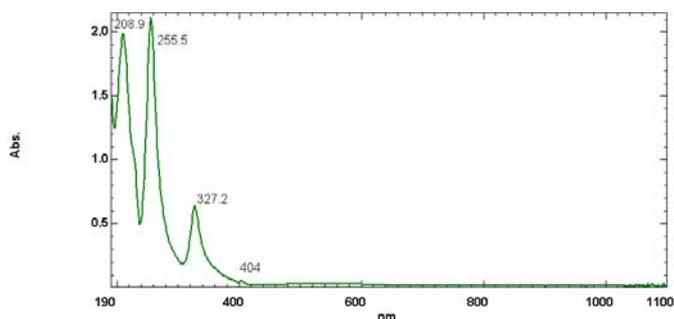


Figure 1. Electronic absorption spectrum in the ultraviolet of C<sub>60</sub> fullerene in n-hexane

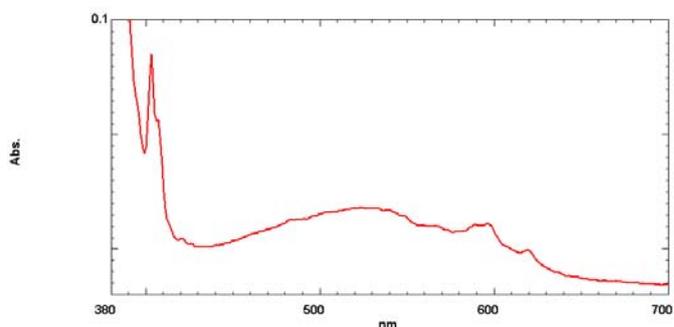


Figure 2. Electronic absorption spectrum in the visible of C<sub>60</sub> fullerene in n-hexane

It was shown that the best solvent having a minimal matrix effect on the band position of the electronic spectra of fullerenes are aliphatic hydrocarbons in general.<sup>10–13</sup> Furthermore, it was shown that the spectra of C<sub>60</sub> and C<sub>70</sub> fullerenes collected in hydrocarbons like for instance hexane or pentane are practically comparable to the expected spectra of fullerenes in the gas phase.<sup>10,11</sup> Thus, we have already (since long time) the instruments for searching neutral fullerenes in the interstellar medium through their electronic absorption bands reference spectra recorded in laboratory and the relative molar extinction coefficients.

### The electronic absorption spectrum of C<sub>60</sub> radical cation

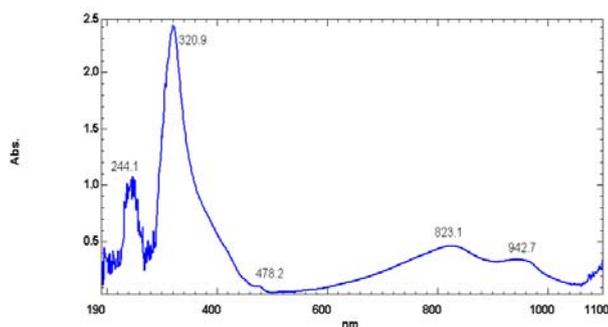
Although a lot of work was done also on the synthesis of the radical cation of C<sub>60</sub> and in recording the relative spectrum, there are not available experimental data on the molar extinction coefficients of the C<sub>60</sub><sup>+</sup> spectrum even if it is thought that it can be detected easier in the interstellar medium than the neutral specie and even if it is also thought that some band of C<sub>60</sub><sup>+</sup> could match one or more diffuse interstellar bands.

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>14–17</sup> Indeed, most works were performed using this technique as comprehensively

reviewed by Reed et al.<sup>18,19</sup> However, none of these works has produced an experimental value of molar extinction coefficient.

There is also another approach to produce radical cations of organic substrates and involves the use of superacids.<sup>18,19</sup> Cataldo was among the first to study the synthesis of  $C_{60}^{+\bullet}$  by dissolving  $C_{60}$  in superacid media consisting either of trifluoromethanesulphonic acid (triflic acid) additionated with potassium persulfate or by using fuming sulphuric acid or oleum with 20-30% free  $SO_3$ .<sup>20</sup> The discussion of the mechanism of oxidation of  $C_{60}$  and  $C_{70}$  in oleum to the respective radical cation and the following reactions with the oxidizing medium is beyond the scope of the present work and has been thoroughly analyzed and discussed in a previous work.<sup>21</sup> Furthermore, there are no doubts about the presence of  $C_{60}^{+\bullet}$  in superacid solutions and this was confirmed by different analytical techniques like electron spin resonance and nuclear magnetic resonance.<sup>18</sup>

In the present work the molar extinction coefficients of  $C_{60}^{+\bullet}$  were determined for the first time. The electronic absorption spectrum of  $C_{60}^{+\bullet}$  is shown in Fig. 3 and it is characterized essentially by two intense bands in the ultraviolet and by two weaker and broad bands in the visible-near infrared. It is interesting to compare the  $C_{60}^{+\bullet}$  spectrum of Fig. 3 with that of the neutral  $C_{60}$  in Fig. 1 (see also Table 1). It appears evident that the intense UV bands of the latter at 209 and 255 nm become a unique band at 244 nm in the spectrum of  $C_{60}^{+\bullet}$ . The molar extinction coefficient of the  $C_{60}$  band at 255 nm is  $\epsilon_{255} = 175000 \text{ L cm}^{-1} \text{ mol}^{-1}$  while the corresponding radical cation band shows an  $\epsilon_{244} = 10296 \text{ L cm}^{-1} \text{ mol}^{-1}$ . Thus, under the radical cation form the UV bands of  $C_{60}$  coalesce into a unique band which shows a reduction of  $\epsilon$  by an order of magnitude in comparison to neutral  $C_{60}$  (see Table 1).



**Figure 3.** Electronic absorption spectrum of  $C_{60}$  radical cation in oleum

Fig. 3 shows the most intense band of the  $C_{60}^{+\bullet}$  spectrum at about 321 nm and this band corresponds to that of  $C_{60}$  at 327 nm but is now blue shifted by 6 nm. Also in this case the molar extinction coefficient which was  $\epsilon_{327} = 51000 \text{ L cm}^{-1} \text{ mol}^{-1}$  for neutral  $C_{60}$ , in the corresponding radical cation was reduced approximately to the half with  $\epsilon_{321} = 28224 \text{ L cm}^{-1} \text{ mol}^{-1}$  (see also Table 1).

In counter tendency, the band at observed at 404 nm in neutral  $C_{60}$  was found at 478 nm in the spectrum of  $C_{60}^{+\bullet}$ , thus considerably red shifted by 74 nm.

**Table 1.** Electronic absorption bands of  $C_{60}$  and its radical cation with the relative molar extinction coefficient values  $\epsilon$

Neutral $C_{60}$		Radical cation $C_{60}^{+\bullet}$	
Wavelength, nm	$\epsilon$ $\text{L mol}^{-1} \text{ cm}^{-1}$	Wavelength, nm	$\epsilon$ $\text{L mol}^{-1} \text{ cm}^{-1}$
208.9	135000	244.1	10296
255.5	175000	320.9	28224
327.2	51000	478.2	n.d.
404.0	n.d.	<b>823.1</b>	<b>7500</b>
530.0	724	<b>942.7</b>	<b>4570</b>

The true radical cation bands of  $C_{60}^{+\bullet}$  are found in oleum at 823 and at 943 nm (see Fig. 3). These are completely new bands and, obviously, have no corresponding band in the spectrum of neutral  $C_{60}$ . The radical cation bands are characterized by a molar extinction coefficient  $\epsilon_{823} = 7500 \text{ L cm}^{-1} \text{ mol}^{-1}$  and  $\epsilon_{943} = 4570 \text{ L cm}^{-1} \text{ mol}^{-1}$ . These values are completely in line with the typical intensity of the radical cation transition of radical cation centered on tertiary carbon atoms.<sup>22</sup>

A summary of all the most relevant electronic absorption bands of  $C_{60}$  in comparison to those of  $C_{60}^{+\bullet}$  are reported in Table 1 where it is possible to appreciate the band shift occurred after oxidation and the changes in the molar extinction coefficients. The new bands highlighted in yellow are due exclusively to  $C_{60}^{+\bullet}$  with the relative  $\epsilon$  values. It is worth reminding here that in oleum  $C_{60}$  first develops the band at about 823 nm with a smaller side band at 943 nm. Then the former band decreases in intensity with time while the latter increases.<sup>21</sup> Consequently, it was concluded that the true radical cation band is that at 943 nm with  $\epsilon = 4570 \text{ L cm}^{-1} \text{ mol}^{-1}$  while the other band at shorter wavelength is essentially due to a charge-transfer interaction of the solute with solvent.<sup>21</sup>

Reed has made a comprehensive summary of the works on the search of radical cation spectra of  $C_{60}$  in various conditions.<sup>19</sup> In general the  $C_{60}^{+\bullet}$  band appears as a singlet at about 980 nm when generated in frozen and inert matrices at low temperatures under high energy irradiation. However, Kato et al.<sup>14</sup> in the discussion of their  $C_{60}^{+\bullet}$  spectrum at 77K generated by  $\gamma$  irradiation of  $C_{60}$  admit the existence of two bands attributable to the radical cation: the main band at 980 nm and a weaker band at about 850 nm. After all, also the CNDO/S calculations on the theoretical spectrum of  $C_{60}^{+\bullet}$  clearly suggest a structure of the true radical cation transition of  $C_{60}^{+\bullet}$  composed by two bands.<sup>14</sup> Indeed two bands were also observed in the spectrum of  $C_{60}^{+\bullet}$  when generated in superacid media.<sup>19-21</sup> For example in  $SbCl_5$  the peaks of  $C_{60}^{+\bullet}$  are found at 850 and 980 nm and in mixtures of  $FSO_3H/SbF_5$  at 766 and 818 nm.<sup>19</sup> As shown in Table 1,  $C_{60}^{+\bullet}$  in oleum shows two bands at about 823 and 943 nm. However, the higher energy transition band in superacid media may be interpreted in terms of solute interaction with solvent as discussed earlier.<sup>21</sup> The spectrum of  $C_{60}^{+\bullet}$  is affected by the medium or matrix where the cation is hosted because of secondary interactions which are able to cause a band shift but should not influence significantly the strength of the transition which, once measured in a given medium can be used – as a first approximation – also for all the other media.

In conclusion, the molar extinction coefficient of the radical cation band of  $C_{60}$  which should be expected between <940 to 980 nm (depending from the polarity of the host matrix, i.e. the environment surrounding the  $C_{60}^{++}$ ) should have a molar extinction coefficient of  $\approx 5000 \text{ L cm}^{-1} \text{ mol}^{-1}$ . A higher energy transition of  $C_{60}^{++}$  expected at about 820-850 nm has a molar extinction coefficient of  $7500 \text{ L cm}^{-1} \text{ mol}^{-1}$  as measured in oleum but may be linked to the solute-solvent charge transfer interaction and could not be a true (or pure) radical cation transition.

### The electronic absorption spectrum of $C_{70}$ fullerene and the radical cation $C_{70}^{++}$

The electronic absorption spectrum of  $C_{70}$  is characterized by two intense transitions at 211 and 234 nm followed by a series of weak electronic transitions at 330, 357 and 376 nm and by a weak and broad band at 466 and 544 nm. The spectrum of  $C_{70}$  in n-hexane is shown in Fig. 4 and the main absorption bands are reported in Table 2 with the relative molar extinction coefficients.

As discussed for  $C_{60}$ , also in the case of  $C_{70}^{++}$  spectrum in oleum only one absorption band is shown in the ultraviolet at 244.1 nm instead of the two bands of neutral  $C_{70}$  located at 211 and 234 nm (see also Fig. 5 in comparison to Fig. 4).

**Table 2.** Electronic absorption bands of  $C_{70}$  and its radical cation with the relative molar extinction coefficient values  $\epsilon$

Neutral $C_{60}$		Radical cation $C_{60}^{++}$	
Wavelength, nm	$\epsilon$ $\text{L mol}^{-1} \text{ cm}^{-1}$	Wavelength, nm	$\epsilon$ (*) $\text{L mol}^{-1} \text{ cm}^{-1}$
211.4	107680	244.1	12600 (*)
234.0	111744	320.9	19250 (*)
329.7	24380	445.5	7800 (*)
357.4		641.8	10400
376.3	28444		
466.9	15166		
544.9			

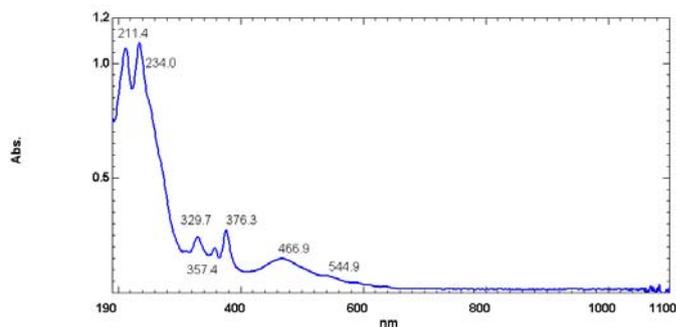
(\*) baseline subtracted

Again, as already admitted for  $C_{60}/C_{60}^{++}$ , the two bands of  $C_{70}$  at 211 and 234 nm coalesce into a unique band at 244 nm in the case of  $C_{70}^{++}$  spectrum (see Fig. 4 and 5). As in the case of  $C_{60}^{++}$ , the molar extinction coefficient of the radical cation band at 244 nm appears reduced by one order of magnitude in comparison to the band of neutral  $C_{70}$  (see Table 2).

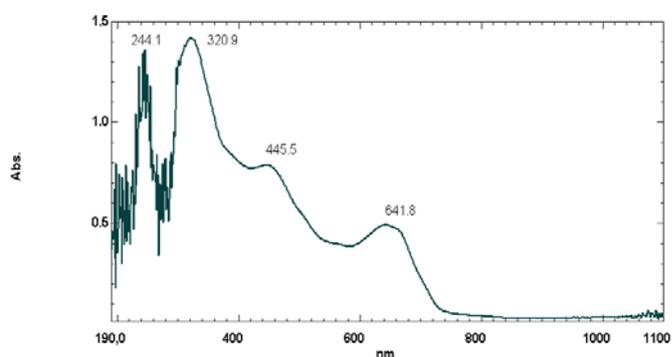
The spectrum of  $C_{70}^{++}$  shows also two transitions at about 321 and 445 nm which appear as the blue shifted bands of neutral  $C_{70}$  originally located at 330 and 467 nm respectively. The mentioned blue shifted bands of  $C_{70}^{++}$  show also a significant reduction of the molar extinction coefficient in comparison to that shown by the original bands in the case of  $C_{70}$  (see Table 2).

The true radical cation band of  $C_{70}$  is located at about 642 nm with an  $\epsilon$  value of  $10400 \text{ L cm}^{-1} \text{ mol}^{-1}$ . The spectrum of  $C_{70}^{++}$  in oleum is in line with earlier results<sup>21</sup> but this time the molar extinction coefficient value of this band has been

determined. The CNDO/S calculations made by Kato et al.<sup>14</sup> on the spectrum of  $C_{70}^{++}$  suggest indeed three main transitions which may appear as bands at 304, 332-349 and 464 nm.



**Figure 4.** Electronic absorption spectrum of  $C_{70}$  fullerene in n-hexane



**Figure 5.** Electronic absorption spectrum of  $C_{70}$  radical cation in oleum

In our spectrum of  $C_{70}^{++}$  of Fig. 5 the above three main transitions appear systematically blue shifted in comparison to the theoretical calculation and located at 244, 321 and 445 nm respectively. The calculation by CNDO/S shows also that for  $C_{70}^{++}$  there are nine symmetry forbidden transitions between 650 and 1300 nm.<sup>14</sup> It is curious that indeed we are finding the true radical cation band of  $C_{70}^{++}$  at 642 nm, just before the region of forbidden transitions.

### Electronic absorption spectroscopy of hydrogenated fullerenes (fulleranes)

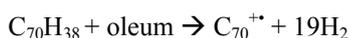
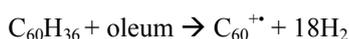
To complete the topic of the molar extinction coefficients of  $C_{60}$  and  $C_{70}$  and their radical cation, in this paragraph we wish to summarize our previous works on other fullerene derivatives of interest in the astrochemical research.

Both  $C_{60}$  and  $C_{70}$  fullerenes are extremely reactive and avid of atomic hydrogen and it was demonstrated experimentally that  $C_{60}$  is transformed very quickly into the fullerane  $C_{60}H_{36}$  when reacted with atomic hydrogen while  $C_{70}$  yields  $C_{70}H_{38}$ .<sup>23,24</sup> The same reactivity is also shown by  $C_{60}$  and  $C_{70}$  with deuterium yielding the deuterated fulleranes analogous to the hydrogenated derivatives mentioned above.<sup>25,26</sup> The  $C_{60}H_{36}$  fullerane displays an electronic absorption spectrum with a unique absorption band at 217 nm with a molar extinction coefficient  $\epsilon=17140$

L cm<sup>-1</sup> mol<sup>-1</sup> while C<sub>60</sub>D<sub>36</sub> shows an analogous spectrum with a maximum at 217 nm and  $\epsilon = 16480$  L cm<sup>-1</sup> mol<sup>-1</sup>.<sup>23,27</sup> It has been shown that the peak of C<sub>60</sub>H<sub>36</sub> matches both in position and in width the UV bump of the interstellar light extinction curve.<sup>23</sup> It is interesting to note that also the hydrogenated and deuterated C<sub>70</sub> under the form of C<sub>70</sub>H<sub>38</sub> and C<sub>70</sub>D<sub>38</sub> display an analogous UV spectrum as that shown by the hydrogenated and perdeuterated C<sub>60</sub> derivatives. The peak position is found at 214 nm with  $\epsilon = 6300$  L cm<sup>-1</sup> mol<sup>-1</sup> in the case of C<sub>70</sub>H<sub>38</sub> and  $\epsilon = 5800$  L cm<sup>-1</sup> mol<sup>-1</sup> in the case of C<sub>70</sub>D<sub>38</sub>.<sup>28</sup> These results imply that hydrogenated and deuterated C<sub>60</sub> and C<sub>70</sub> fullerenes can be present in the interstellar medium and may contribute to the UV bump of the interstellar light extinction curve and may play a key role in molecular hydrogen formation in space starting from the atomic hydrogen adsorption on the fullerene cage structure and release as molecular hydrogen under UV irradiation.<sup>24</sup> Indeed, it was shown experimentally<sup>23,27,28</sup> that the UV irradiation of fullerenes, the hydrogenated fullerenes, causes the release of molecular hydrogen and the consequent partial dehydrogenation of the fullerene with a shift of the electronic transition at 217 nm toward longer wavelengths. Another characteristic property of hydrogenated/deuterated fullerenes regards the kinetic isotope effect observed experimentally during the photolysis, which involves an easier photolysis of the C-H bond in comparison to the C-D bond with the consequent possible H/D fractionation on the fullerene surface.<sup>23,27,28</sup>

#### About hydrogenated fullerenes radical cation

When hydrogenated C<sub>60</sub> and C<sub>70</sub> are dissolved in the same medium that generates C<sub>60</sub><sup>•+</sup> and C<sub>70</sub><sup>•+</sup>, it happens that they undergo an almost complete dehydrogenation, displaying once again the bands of the radical cation spectra of the original fullerenes.<sup>26,29</sup>



#### Search for radical cation spectra of higher fullerenes

An attempt to record the radical cation spectra of higher fullerenes like C<sub>76</sub>, C<sub>78</sub> and C<sub>84</sub> in oleum was also made but the results show only weak and broad transitions in the near infrared that may suggest that higher fullerenes once oxidized to the radical cation stage undergo further oxidative decomposition (at least in oleum).<sup>30</sup>

#### CONCLUSIONS

The radical cation species C<sub>60</sub><sup>•+</sup> and C<sub>70</sub><sup>•+</sup> were generated in oleum and the resulting complete electronic absorption spectra in the spectral range comprised between 190 and 1100 nm were recorded. For the first time the molar extinction coefficient of the main absorption bands of the radical cations C<sub>60</sub><sup>•+</sup> and C<sub>70</sub><sup>•+</sup> were measured and compared with the absorption bands and molar extinction coefficients

of the spectra of neutral C<sub>60</sub> and C<sub>70</sub> recorded in n-hexane. Furthermore, for the sake of completeness, the electronic absorption spectra and the relative molar extinction coefficients of hydrogenated and perdeuterated fullerenes (fulleranes) were reported as well including the behavior of fulleranes and higher fullerenes in oleum.

The data presented in the present work are of key importance in the search, identification and quantification of fullerenes, their radical cation and fulleranes in the interstellar medium since we already know that fullerenes and derivatives may be ubiquitous in the Universe.

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