

# Spectroscopy of Fullerenes, Fulleranes and PAHs in the UV, Visible and Near Infrared Spectral Range

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**Abstract.** The spectra of fullerenes C<sub>60</sub> and C<sub>70</sub>, higher fullerenes C<sub>76</sub>, C<sub>78</sub> and C<sub>84</sub> and hydrogenated fullerenes (fulleranes) were studied in laboratory in the UV and in the visible spectral range and could be used for searching and recognizing these molecules in space. Furthermore, the radical cation spectra of all the mentioned fullerene series and also of a series of large and very large polycyclic aromatic hydrocarbons (PAHs) were generated in the laboratory and studied in the near infrared spectral range.

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C<sub>60</sub> and C<sub>70</sub> fullerenes display quite complex spectra in the ultraviolet and visible spectral regions due to the electronic transitions of the  $\pi$  electrons of their weakly conjugated double bonds. C<sub>60</sub> shows two intense bands at 213 and 257 nm, respectively, with a molar extinction coefficient  $\varepsilon$  of 135000 and 175000 L cm<sup>-1</sup> mol<sup>-1</sup>, respectively. Other bands of C<sub>60</sub> appear at 329 nm ( $\varepsilon = 51000$  L cm<sup>-1</sup> mol<sup>-1</sup>), 404 nm and a broad and relatively weak band between 440 and 670 nm with subfeatures at 500, 540, 570, 600 and 625 nm. Similarly, also the electronic absorption spectrum of C<sub>70</sub> is characterized by two intense transitions at 210 and 228 nm followed by a series of weak electronic transitions at 327, 358 and 375 nm and by a weak and broad band at 460 nm. Both C<sub>60</sub> and C<sub>70</sub> fullerenes are extremely reactive and avid of atomic hydrogen and it was demonstrated experimentally that C<sub>60</sub> is transformed very quickly into the fullerane C<sub>60</sub>H<sub>36</sub> when reacted with atomic hydrogen while C<sub>70</sub> yields C<sub>70</sub>H<sub>38</sub> (Cataldo & Iglesias-Groth 2009, 2010). The same reactivity is also shown by C<sub>60</sub> and C<sub>70</sub> with deuterium yielding the deuterated fulleranes analogous to the hydrogenated derivatives mentioned above (Cataldo *et al.* 2009a,b). The C<sub>60</sub>H<sub>36</sub> fullerane displays an electronic absorption spectrum with a unique absorption band at 217 nm with a molar extinction coefficient  $\varepsilon = 17140$  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  $\varepsilon = 16480$  L cm<sup>-1</sup> mol<sup>-1</sup> (Cataldo & Iglesias-Groth 2009; Cataldo *et al.* 2009c). 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 (Cataldo & Iglesias-Groth 2009). 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  $\varepsilon = 6300$  L cm<sup>-1</sup> mol<sup>-1</sup> in the case of C<sub>70</sub>H<sub>38</sub> and  $\varepsilon = 5800$  L cm<sup>-1</sup> mol<sup>-1</sup> in the case

of  $C_{70}D_{38}$  (Cataldo *et al.* 2009d). These results imply that hydrogenated and deuterated  $C_{60}$  and  $C_{70}$  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 (Cataldo & Iglesias-Groth 2010). Indeed, it was shown experimentally (Cataldo & Iglesias-Groth 2009; Cataldo *et al.* 2009c,d) that the UV irradiation of fullerenes, the hydrogenated fullerenes, causes the release of molecular hydrogen and the consequent partial dehydrogenation of the fullerane 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 (Cataldo & Iglesias-Groth 2009; Cataldo *et al.* 2009c,d).

In the interstellar medium under the action of cosmic rays or other radiation,  $C_{60}$  may undergo ionization losing one electron and yielding a radical cation. In laboratory the radical cation spectrum of  $C_{60}$  was produced in a very high oxidizing medium known as oleum (Cataldo *et al.* 2012a) and the resulting electronic transitions were found in the near-infrared at 823.7 nm and at 931.5 nm. The latter transition was interpreted as the true radical cation transition of  $C_{60}$ . On the other hand, under the same conditions the radical cation of  $C_{70}$  displays its longest wavelength transition at about 640 nm (Cataldo *et al.* 2012a). When hydrogenated  $C_{60}$  and  $C_{70}$  are dissolved in the same medium that generates  $C_{60}^{+\cdot}$  and  $C_{70}^{+\cdot}$ , it happens that they undergo an almost complete dehydrogenation, displaying once again the bands of the radical cation spectra (Cataldo *et al.* 2009b, 2012b):  $C_{60}H_{36} + \text{oleum} \rightarrow C_{60}^{+\cdot} + 18H_2$  and  $C_{70}H_{38} + \text{oleum} \rightarrow C_{70}^{+\cdot} + 19H_2$ .

An attempt to record the radical cation spectra of higher fullerenes like  $C_{76}$ ,  $C_{78}$  and  $C_{84}$  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) (Cataldo *et al.* 2012a).

Although less probable than the radical cation formation, it is expected that in space  $C_{60}$  and  $C_{70}$  fullerenes may produce also the radical anion (Cataldo *et al.* 2013a). The radical anion spectrum of  $C_{60}$  is characterized by a complex band pattern, showing a series of peaks at 935, 994, 1032 and 1058 nm while the radical anion spectrum of  $C_{70}$  shows only a broad band with a peak in the range comprised between 814 and 840 nm.

The infrared spectra of a series of reference fullerenes and fullerenes have been recorded in the laboratory by Iglesias-Groth *et al.* (2011, 2012) together with the relative molar absorptivity. This recent laboratory spectroscopy of  $C_{60}$  and  $C_{70}$  fullerenes has permitted an accurate determination of the fullerene abundances in space (García-Hernández *et al.* 2011, 2012). In addition, because the reference spectra of hydrogenated fullerenes (fullerenes) are now available, a search for these molecular species can now be made in space, and their possible detection in astrophysical environments may be only a matter of time and luck.

Very large polycyclic aromatic hydrocarbons (VPAHs) are not easily accessible but of high interest as reference molecules for the explanation of the diffuse interstellar bands (DIBs). Using the Scholl reaction, Cataldo *et al.* (2011) have synthesized a series of VPAHs, ranging from dicoronylene to quaterrylene to hexabenzocoronene. Dicoronylene was also obtained by the thermal dimerization of coronene. If the thermal treatment of coronene is prolonged, then the oligomerization of coronene proceeds further, yielding a

black oligomer, which is probably a trimer or a higher homologue. It is shown that from coronene oligomerization it is possible to build a sheet of graphene.

The radical cation spectra of a series of normal PAHs and VPAHs were studied by Cataldo *et al.* (2010) using oleum as oxidizing medium. PAHs and VPAHs in the harsh space conditions are expected to undergo ionization, being mainly in the form of radical cations. The radical cation spectra of PAHs and VPAHs are characterized by intense electronic transitions, which in our laboratory conditions appear as relatively broad bands but in the gas phase and at relatively lower temperature such electronic transition must appear as sharp and narrow bands. Thus, it is possible that some DIBs could be associated to the radical cation transitions of some PAHs or, even better, to some VPAHs. It could be useful to mention here some of the results reported in the work of Cataldo *et al.* (2010). First of all the PAHs and VPAHs once oxidized to the radical cation display electronic transitions in the visible and in the near infrared and may be associated to certain DIBs. The anthracene radical cation shows its longest wavelength transition (LWT) at 588.2 nm, tetracene radical cation LWT = 652.8 nm, pentacene radical cation LWT = 760.4 nm, pyrene radical cation LWT = 556 and 602 nm, coronene radical cation LWT = 574 nm, dicoronylene radical cation LWT = 755 nm, coronene oligomer radical cation LWT = 881 nm, perylene radical cation LWT = 515 nm and quaterylene radical cation LWT = 811 and 838 nm. Finally, far infrared spectroscopy on a series of PAHs, VPAHs and petroleum and coal fractions were also reported in recent works by Cataldo *et al.* (2013b,c).

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