ESR Study on the Doublet and Triplet Species Present in Pristine C_{60} Fullerene Powder

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Doublet and triplet magnetic species have been detected and studied by ESR spectroscopy in the pristine fullerene C_{60} both in the solid state and in solution. It has been confirmed that the doublet species take origin from a photon-assisted reaction with the molecular oxygen O_2 of the air. Anyway, from T_1 relaxation-time measurements and from physical treatment of the samples, it has been established that the doublet species are not really in solution, but they are contained in the bulk of diamagnetic clusters suspended in the employed solvent. The magnetic interaction between the doublet species has also been detected and it allowed to obtain the mean distance between two of the interacting radical ions which are supposed to be $(C_{60}{}^{+})^{\bullet}$ species.

Introduction

Fullerenes have become recently of growing importance in the field of the material sciences, and they are presently stimulating more and more interest in employing them as starting precursors toward the chemical synthesis of new derivatives.[1] For this reason it seemed us worth giving a contribution to the characterization of what we call the "pristine" powder of fullerene C_{60}, i.e., the powder of C_{60} so as it is obtained from its synthesis or it is purchased on the market.

It is our experience that anytime a powder of C_{60} is examined under electron spin resonance (ESR) conditions, a single resonance line having a width of about 0.12 mT and a g factor of 2.0026 ± 0.0002 can be detected at the X-band (from 9 to 10 gHz). This line is always present independently from the source of the pristine powder (from the trade or homemade), only its intensity being variable from a sample to another. Moreover, also when the powder is dissolved in a solvent like toluene, ESR active doublet species can be detected in the solution. On the other hand, it is well-known that the C_{60} molecule is a diamagnetic one when it is in its singlet ground state. The presence of radical species in a C_{60} solution when used as a starting ingredient to synthesize variously substituted fullerene derivatives or superconducting materials could influence the behavior of the solution itself and/or the nature of the obtained products. The aim of this study was to contribute to clarify the nature of those species and to find a way of obtaining solutions free from ESR-active species.

Experimental Section

The ESR spectra were recorded by a ER 200D-SRC Bruker spectrometer provided with a ER 4111 VT variable-temperature unit. The C_{60} samples were homemade by the electric discharge method[2] or purchased from Aldrich (USA). Soot containing fullerenes, obtained by the arc method, was extracted with benzene and C_{60} powder purified by liquid chromatography.[2] The purity, which was verified by IR and Raman spectroscopy, was better than 99%. The sample purchased from Aldrich, listed as buckminsterfullerene to distinguish it from a different item listed as fullerite (a mixture C_{60}/C_{70} = 10:1), was not further characterized. The toluene used as the solvent (99.5%, Carlo Erba, Italy) was used without further purification after having verified its ESR inactivity.

Samples of about 44 mg in weight were solubilized in about 500 μL of toluene, obtaining a dark red-wine coloured solution which appeared turbid due to macroparticles suspended in it. A part of the powder of C_{60} appears always to be insoluble though the volume is increased up to some milliliters and the solution is vigorously stirred for several hours. The effect is more marked if the powder has not been freshly prepared.

The filtration of the toluene solutions was performed by using nylon filters (1.5 cm in diameter) having meshes of 0.45 μm, contained in a stainless steel holder, connected to the top of a glass syringe.

Discussion

(a) C_{60} Powders and Toluene Solutions As-Prepared. Figure 1 shows the different ESR lines detected when C_{60} powders or solutions are considered. Figure 1a shows a typical resonance line representative of a C_{60} powder sample. The intensities (the areas) of the ESR lines of the different pristine powders coming from different sources correspond to a content of doublet species which spreads from a few up to about a thousand parts per million. The content was evaluated by comparing the intensities of the C_{60} lines to the intensity of a reference solid solution having a known content of paramagnetic nitroxide N–O group. A solution as-prepared in toluene gives exactly the same resonance line; as mentioned, the as-prepared solution appears dark red-wine colored, turbid and often with a black

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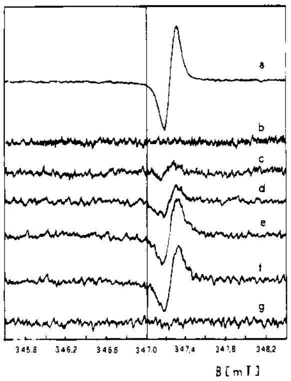

Figure 1. ESR signals obtained for different samples of C_{60}. (a) C_{60} pristine powder; (b) the disappearance of the ESR signal when the dark red-wine colored solution is filtered by a 0.45-μm meshes nylon membrane; (c–f) the growing of the ESR signal when the magenta colored solution is exposed to the ambient light; (g) a new filtration purifies again the C_{60} solution (see text).

precipitate at the bottom of the vial. If this solution is filtered with normal filter paper, the precipitate is easily separated, its color is dark brown and it is ESR active. The solution so obtained is now transparent, the color being still dark red-wine. It has been found that this solution still shows the ESR signal whose intensity is lower than that of the solution containing the turbidity and the precipitate. But, as Figure 1b clearly reports, when this dark red-wine transparent solution is filtered by the already cited 0.45-μm nylon membrane, the solution becomes magenta colored and its ESR signal totally disappears. The nylon membrane is now brownish colored after careful washing with toluene and when introduced into the ESR spectrometer gives exactly the same ESR line shape obtained from the previous precipitate and from the red-wine solution. Its intensity is better comparable to that of the solution rather than to that of the precipitate which usually gives an ESR line which is the most intense. On the other hand, these findings bring us to sustain the hypothesis that the doublet species are not really in solution as isolated species, the nature of which has to be identified. The fact that the filtration by the 0.45-μm nylon membrane changes completely the color of the solution from red-wine to magenta and that the ESR signal totally disappears, pushes us to believe that microclusters larger than 0.45 μm are suspended in the toluene solution. These microclusters, clearly much larger than a single fullerene molecule having a diameter of about 7 Å, represent the first step in the process leading to the formation of the precipitate which can be separated by a normal filter paper. Both the microclusters and the precipitate are essentially diamagnetic in nature but they must include in themselves the doublet species which give the ESR signal. For a better morphological characterization of the microclusters in solution, we are now doing Raleigh scattering experiments. At the same time, light absorption measurements will be performed to clarify how the microclusters in solution can affect the color of the solution from magenta to red-wine. An answer to this question could contribute to elucidate the nature of the species setting up the microclusters at the light of some hypotheses we are now going to make.

(b) Effect of the Air and of the Light. As Figure 1c shows, the magenta colored solution develops an ESR signal by simply leaving it inside the ESR sample vial and being exposed to the usual light of the laboratory and to the air. The weak ESR signal developed after an exposure of 10 days corresponds to a content of doublet species of about 20 parts per million. After 10 more days, the ESR signal intensity is clearly doubled (Figure 1d). If the same solution is exposed to a standard light source which can be indifferently an incandescent or a neon lamp, the ESR signal intensity is further tripled after only 10 h more (Figure 1e). At this point, the sample vial has been placed in the dark inside the microwave cavity of the EPR spectrometer and held there 7 days more, the solution being exposed to the air as before. As Figure 1f shows, in these conditions the ESR signal intensity and the quantity of doublet species remains absolutely constant and of the order of 100 parts per million. During all this time the color of the solution changed progressively from the initial magenta color to the red-wine color of the solution of Figure 1e and 1f. These solutions are neither turbid nor present a precipitate but, when again filtered by the 0.45-μm nylon membrane, they are totally lacking ESR signal and become magenta colored again (Figure 1g).

All these findings seem to confirm the hypotheses made in a recent paper[3] about the photochemical origin of the doublet species seen by ESR. In that paper, a 500-W Xe lamp was used; we have also found that in the natural light level of a laboratory, a nonnegligible amount of doublet species can be formed both during the synthesis and the following handling of C_{60} powders and solutions. We can now assert that the photochemical process is to be identified in the reaction between one of the excited states of C_{60} and the molecular oxygen O_2 of the air. The C_{60} molecule can be very easily excited by the visible light and this explains why we have found that a Xe lamp is not necessary. Other evidences have frequently stressed that fullerene evolved its behavior during an experiment under optical irradiation and in the presence of air.[4] On the other hand, the final products of the photoreaction between C_{60} and O_2 should be singlet species and consequently diamagnetic ones. Oxygenated derivatives of C_{60} had already been obtained by photochemical reaction and studied by infrared spectroscopy.[5] They imply the cleavage of a C–C bond and the formation of C–O bonds. More recently, a $C_{60}O$-type derivative of fullerene has been theoretically studied.[1] On these bases, to contribute to the understanding of the nature of the doublet species seen by ESR, we make the hypothesis that the molecular entities giving origin to the diamagnetic clusters which tend to become insoluble in the toluene may be the oxygenated derivatives of C_{60}. The same species would change the spectral absorption of fullerene from magenta to red-wine color. Due to the fact that the photochemical reaction with O_2 goes with high probability through intermediate states characterized by unpaired electrons (triplet or doublet ones), it is reasonable to suppose that the ESR active species can represent a step of such reaction. In some cases the photo-

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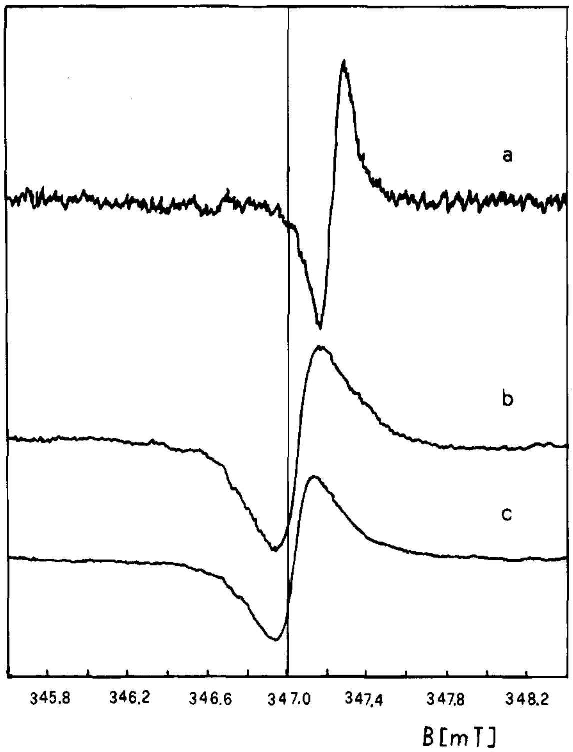

Figure 2. ESR signals from a toluene solution of C_{60} (a) and from a suspension in toluene of Darco T70 (b) and Darco KB (c) carbon blacks. As in Figure 1, the position of the central vertical segment corresponds to $g = 2.0037$ of DPPH. The C_{60} signals are located at $g = 2.0026$. The two Darco carbon blacks give signals at $g = 2.0034$.

chemical reaction would remain frozen at a stage which could generically be represented as $^{\bullet+}C_{60}$–O_2, a radical cation which is well-known to exist in the graphite.[6,7] The probability that the radical cation remains trapped and stable in the lattice of the oxygenated C_{60} is not high as shown by the relatively few parts per million of doublet species detected by ESR both in the powders and in the solutions. The value of $g = 2.0026 \pm 0.0002$ found for all our samples fits well with the values around $g = 2.0030$ found and foreseen[8,9] for the radical cation $^{\bullet+}C$ in graphite. To provide further evidence, we have made ESR spectra of two typical Darco carbon blacks as powders suspended in toluene. As Figure 2 shows, the two carbon blacks actually have $g = 2.0034$, even if the linewidths (0.21 mT) are broader than that of the fullerene derivative (reported for comparison) thus reflecting perhaps the major difference in the interactions with the rest of the lattice of the two $^{\bullet+}C$ radicals. As we will see in the following paragraph, the relaxation-time measurements will evidence this difference in a well clear way.

(c) T_2 and T_1 Relaxation-Time Measurements. The T_2 value can be very easily obtained by considering that the ESR signals of all powders and solutions we have studied can be well fitted by a lorentzian function. The peak-to-peak linewidth Δpp can be written

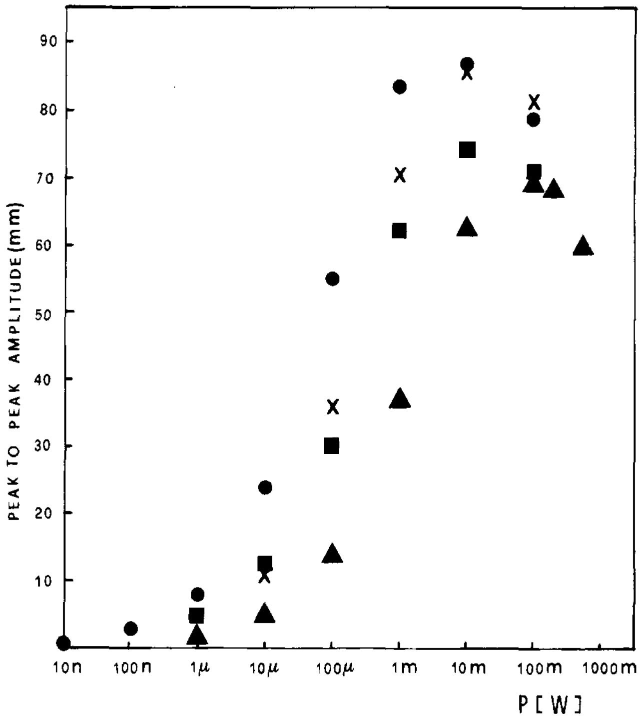

Figure 3. Dependence of the ESR line amplitude on the applied microwave power P for different C_{60} samples. (●), pristine powder; (×), powder on nylon membrane filter; (■), powder from total evaporation of a toluene solution; (▲), toluene solution (see text).

$$\Delta pp = h/(\sqrt{3} g_e \beta_e T_2) \tag{1}$$

with $h = 1.0546 \times 10^{-27}$ erg s; $g_e = 2.002\,32$; $\beta_e = 9.2721 \times 10^{-21}$ erg G^{-1}. By remembering that $\Delta pp = 0.12$ mT for all ESR lines, $T_2 = 2.73 \times 10^{-8}$ s is calculated.

The T_1 values can be deduced from saturation experiments on the different samples taken into consideration. It is necessary only to estimate the value of the microwave field H inside the cavity that is able to saturate the resonance line. At this value of H, H_{max}, the line amplitude does not increase anymore when the microwave power, P_{max}, is further increased. H_{max} can be estimated from the relationship[10]

$$H_{max} = 2.8 \times 10^{-2} (Q P_{max})^{1/2} \tag{2}$$

in which $Q = 4000$ is an estimated value of the merit factor of the employed standard rectangular cavity. Figure 3 reports the dependence of the line amplitudes of the different samples on the applied microwave power P. From the experimentally obtained trends, the values of P_{max} to be introduced in eq 2 (see figure caption) are easily obtained. Once the H_{max} values are available they can be used in

$$T_1 T_2 = 2/(\gamma_e H_{max}) \tag{3}$$

to calculate the T_1 relaxation times, being the T_2 time already known.[10] $\gamma_e = 1.7608 \times 10^7$ rad (s G)$^{-1}$. The deduced T_1 values are reported in Table 1. It is perhaps

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Table 1. T_1 Relaxation Times (microseconds) from ESR Saturation of Different C_{60} Species

pristine powder	powder on filter	powder from evaporation	toluene solution
25.11 ± 0.2	2.52 ± 0.2	2.55 ± 0.2	1.51 ± 0.2

meaningful that C_{60} as pristine powder has a $T_1 = 25.1$ μs value which is a fairly long one on the ESR scale of times. The longest T_1 time could reflect the fact that in the pristine powder the ESR active species are embedded in clusters having the largest sizes. The freshly obtained powders collected on the nylon filter or by complete evaporation of a toluene solution (in the presence of air and light) have T_1 times of the order of 2.5 μs. The toluene solution having a red-wine color (before the filtration) has a $T_1 = 1.5$ μs time that is comparable with that of the two previous powders. This last result confirms, in our opinion, that the ESR signal arises from species which are embedded in a solid-state matrix and not really in solution. Indeed a species in solution usually has a T_1 time which is shorter and of the order of T_2, i.e., of the order of 10^{-8} s. We have also tried to obtain the T_1 value for the two Darco carbon blacks of which the ESR lines are reported in Figure 2. The two T_2 values, being $\Delta pp = 0.21$ mT for both lines, are easily obtained from eq 1 and amount to 1.56×10^{-8} s, a value which is not so far from that obtained for the fullerenic species. On the other hand, the dependence of the ESR line amplitudes on the microwave power showed no trend toward a maximum also at the greatest power of our klystron which is of the order of 500 mW. This means that the T_1 values of the carbon black species are at least one order of magnitude shorter than the T_1 values that we have determined for the fullerenic species. The short T_1 relaxation times for the carbon black species clearly reflect the more efficient relaxation pathways of these species which are known to be connected through C−C chemical bonds to the rest of the lattice. The molecule of fullerene, on the contrary, is known to be free of rotating at its lattice site, at room temperature.[11,12] In this situation, a hypothetical fullerenic ESR-active species maintaining the spherical symmetry of neutral fullerene could be foreseen to have a very long T_1 time due to the very weak interactions with the rest of the lattice. It is possible that our hypothised fullerenic $^{\bullet+}C_{60}{}^{\bullet-}O_2$ species in the diamagnetic matrix of oxygenated C_{60} maintain interactions sufficiently weak so that to justify T_1 relaxation times longer that those measured in carbon blacks. It remains to say that preliminary measurements on the temperature dependence of the T_2 and T_1 relaxation times of the fullerenic species seem to indicate that, at least down to 100 K, they remain nearly unchanged.

(d) Magnetic Interactions between Doublet Species. When the ESR line of a pristine C_{60} powder is observed at a higher gain (×10) of the spectrometer, it becomes evident that two small components appear in symmetrical positions with respect to the center of the line itself (Figure 4). These two lateral components are always present in all the studied samples of pristine powder, but their amplitude with respect to that of the central line was largely variable. In some samples, additional splittings were evident but hardly measurable due to their closeness to the center of the ESR line. We have made the hypothesis that the lateral components take origin from a dipole magnetic interaction between unpaired electrons located on two different $^{\bullet+}C_{60}{}^{\bullet-}O_2$ species. The measured splitting between the two lateral components amounts to $2D = 1.1$ mT. The magnetic interaction in this formally triplet species can be described in the frame of a point-dipole approach. The isotropic exchange term J and the anisotropic term E with nonaxial symmetry are considered to be equal to zero. The only surviving term is that describing an anisotropic interaction with axial symmetry which is called D and which corresponds to half of the measured splitting. In this approach[13] the distance r between the unpaired and localized electron charges can be evaluated from

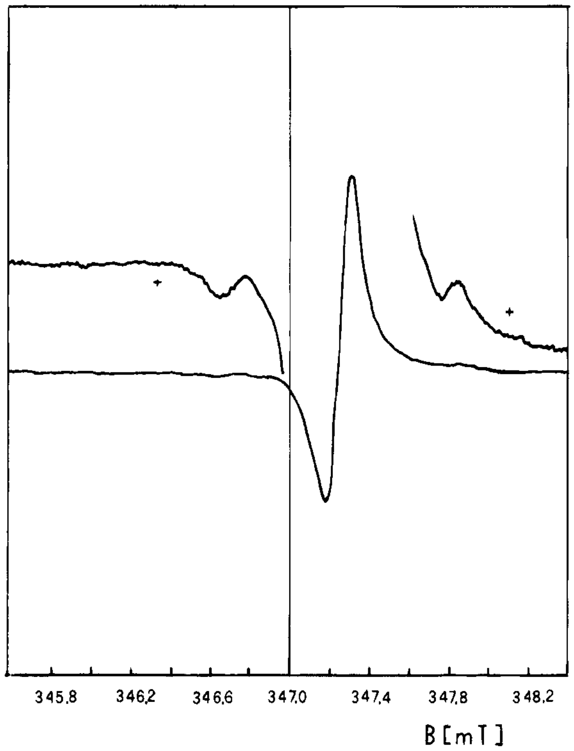

Figure 4. ESR signal of pristine powder of C_{60}. The trace marked + shows the lateral symmetric components at a higher gain (×10) of the spectrometer. The splitting between the lateral components is $2D = 1.1$ mT.

$$D = 3g_e\beta_e/2r^3 \tag{4}$$

r being obtained in angstroms if D is given in gauss. By introducing the already used values of g_e and β_e, a value of the distance is obtained which amounts to $r = 17.17$ Å. From the face-centered-cubic (fcc) lattice structure of C_{60} at room temperature,[11,14] we know that the distance between the centers of two adjacent C_{60} balls on the side of the cube is equal to 10.0 Å. We also know that the mean radius of each C_{60} ball is equal to 3.55 Å. Therefore, the determined distance $r = 17.17$

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Å corresponds surprisingly well to that between two electron charges localized on the opposite sides of those two C_{60} balls. The result seems reasonable if we admit that the steric hindrance and the electrostatic repulsion between the two oxygens of the two radical cations $^{\bullet+}C_{60}-O_2$ favor this opposite-side geometry. To sustain these considerations, it is also necessary to admit that the lattice structure of the oxygenated C_{60} clusters in which the radical cations are trapped is not too different with respect to that of the C_{60} itself. The electrostatic and steric hindrances seem also to inhibit the formation of doublet species along the diagonal of a face of the cube at a distance of 7.05 Å between the centers of two C_{60} balls one of which being on the edge of the cube and the other one at the center of the face of the cube. As a matter of fact, no hints of lateral components of the ESR line appear to the corresponding $D = 2.4$ mT value. All other additional lateral components having D values lower than 0.55 mT can arise from other couples of doublet species being at distances larger than 17.17 Å. Distances of 21 and 24 Å can, for instance, be assigned to couples being at the extremity of the diagonal of a face and of the cube, respectively. The calculated D values are 0.30 and 0.20 mT which roughly correspond to the inflections often seen on the ESR lines but with their splittings hardly measurable. The relative intensities of all these lines possibly depend on the former history of the studied sample with regard to its synthesis and its exposition to the air and to the light. It remains to say that from a consideration of the relative intensities of the ESR central line and of the lateral components at $D = 0.55$ mT, the abundance of this triplet species can be evaluated, at least for this sample, to be one-hundredth of that of the radical cation.

Conclusions

We have given a contribution to the detection and to the characterization of magnetically active species preexisting in those we have called "pristine" powders of C_{60}, before any chemical utilization. Having clarified the nature of those species will be of help in understanding the behavior of solutions of C_{60} when examined by optical methods. Alternatively, it will simplify the interpretation of results obtained on fullerenic materials, like for instance the superconductors, by assigning some detected magnetic signals[15] to species preexisting to the formation of the superconductor itself. More in general, we have indicated a way to test a C_{60} powder or solution in order to evidence its magnetic state and, what is perhaps more important, to dispose of a simple method of filtration to purify the solution in view of the future chemical utilizations.

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