Pulsed EPR and ^{13}C NMR: Complementary Tools on the Study of Solid C_{60} Fullerene

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Abstract: A correlation between independent ^{13}C NMR (Belahmer et al.) and pulsed EPR measurements on air-exposed polycrystalline C_{60} samples is observed. The recently introduced PEANUT (acronym for Phase-inverted Echo-Amplitude detected NUTation) pulse scheme was employed to get deeper insight on the study of the nature of the paramagnetic species of pristine fullerene powder. The origin of the spectral lines seem in the EPR spectrum of solid C_{60} is determined: they arise from the interaction between the π electrons of the outer surface of the fullerene molecules and of the oxygen molecules intercalated into the voids of the fullerene crystal lattice. The aim of this report is to establish and demonstrate the complementary of the two magnetic resonance techniques on the study of solid fullerenes.

Resumo: É apresentada uma correlação entre medidas independentes de RMN [13]C (Belahmer et al.) e de RPE pulsada em amostras de C_{60} policristalino expostas ao ar. A recém introduzida seqüência de pulsos PEANUT (acrônimo de Phase-inverted Echo-Amplitude detected NUTation) é usada para aprofundar os estudos sobre a natureza das espécies paramagnéticas do fulereno sólido. A origem das linhas espectrais observadas no espectro de RPE é determinada: elas surgem da interação entre os elétrons π da superfície externa das moléculas de fulereno e das moléculas de oxigênio intercaladas nos interstícios do retículo cristalino do fulereno. O objetivo deste relato é estabelecer e demonstrar a complementaridade das duas técnicas de ressonância no estudo de fulerenos no estado sólido.

Introduction

Discovered serendipitously in 1985, the fullerenes are the third allotrope form of carbon.[1] Amongst its proposed applications are production of organic superconductors, catalysts and nanostructured systems.[2] The most abundant fullerene is C_{60}, icosahedral symmetry. This fullerene crystallises in *fcc* structure, with lattice parameter of 14.4 Å. It is worth of note that in this lattice the fullerene molecules occupy only 2/3 of the apparent volume, leaving voids with octahedral symmetry of a dimension large enough to accommodate most of the chemical elements.[3] Production of intercalation compounds, namely the superconductors A_3C_{60} (where A denotes an alkali metal) is the most evident result of this feature. Although the emphasis in C_{60} research has shifted to the search for high-temperature superconductivity in alkali metal doped fullerides, a detailed knowledge of the C_{60} ordered crystal structure, its defects or impurities should improve understanding of the properties of fullerenes and fullerides.

Recently it has been reported the spontaneous intercalation of molecular oxygen into the lattice voids of C_{60} crystal. The interaction is effective even at room temperature and pressure, and thermal treatments carried out to increase the molecular diffusion induced, on the contrary, irreversible chemical reactions. Due to the paramagnetic nature of the O_2 molecule, the contact interaction between C_{60} π and oxygen orbitals produces a small shift in the solid state ^{13}C NMR, whose amplitude is proportional to the magnetisation, accordingly to the Curie law.[4]

Both in molecular or solid form, C_{60} represents an ideal system for ^{13}C NMR investigations. At room temperature, all 60-carbon atoms are equivalent, and yield a single resonance at δ 143.7 (from TMS). Accordingly, due to the weak Van der Waals intermolecular interactions in the solid, a unique resonance is observed in MAS experiments.[5] This uncommon condition makes ^{13}C NMR particularly attractive since any chemical modification on the fullerene cage itself or any intercalation into the crystalline structure can, at least in principle, be detected by this spectroscopy.

The fullerene-oxygen interaction can also be investigated by EPR. In spite of the fact that the fullerene molecule is diamagnetic, even high-purity samples show EPR lines at room temperature. The spectrum is composed by an intense line around g ~ 2.0026 ± 0.0002, line width about 0.12 mT, flanked by two weak lines with the same g-factor and line width of ~ 1.2 mT. In general, the literature assigns these lines to the contamination by oxygen.[6(a),6(b)] However, none of the existing reports clearly

establish the origin of those EPR lines. For example, when a freshly prepared C_{60} thin film is exposed to air, there is an increase in the number or paramagnetic centres, as shown by EPR measurements. However, the effect depends on the crystalline properties of the film, suggesting that this is not a superficial effect only.[7] Thus, studies of oxygen contamination on fullerene crystals may lead to a better understanding of this process.

In this work we present a correlation between independent ^{13}C NMR (Belahmer *et al.*, Ref. 4) and pulsed EPR measurements on air-exposed polycrystalline C_{60} samples. The recently introduced PEANUT (acronym for Phase-inverted Echo-Amplitude detected NUTation) pulse scheme is employed to get deeper insight on the paramagnetic species formed in pristine fullerene powder. The aim of this report is to establish the origin of the spectral lines seem in the EPR spectra of solid C_{60} and demonstrate the complementary of the two magnetic resonance techniques on the study of solid fullerenes.

The PEANUT experiment

The PEANUT experiment is a two-pulse spin-echo sequence proposed by Jeschke *et al.*[8] The refocusing second pulse is a high turning angle (HTA) pulse of length **T** divided into two parts of lengths **t** and **T-t** with opposite phases of 0 and π respectively. The pulse scheme is illustrated in Figure 1.

The PEANUT technique is based on the proportionality between the transition moment and the frequency at which the electron nutates under resonant microwave radiation. The transient electron spin nutation frequencies are measured *via* an electron spin-echo detected rotary echo. Nutation frequencies are related to *g*-values and electron-spin multiplicity, and can be used to identify species with or without hyperfine interactions.

Concerning the application of the PEANUT pulse sequence to the study of the nature of the EPR spectra of solid fullerenes, two aspects are worth of note: (1) this pulse scheme is suitable for EPR spectra with small frequency range and narrow lines; (2) as the total length of the pulse sequence is kept constant, the influence of relaxation processes is the same during data acquisition. In other words, there is no relaxation broadening. Besides that, a 2D-PEANUT experiment can be performed in order to correlate echo amplitude as a function of time **t** and external magnetic field positions. As described in Ref. 8, cross-sections of the contour plot obtained this way are *nutation frequency selective EPR spectra*, and are equivalent to the echo-detected EPR spectra.
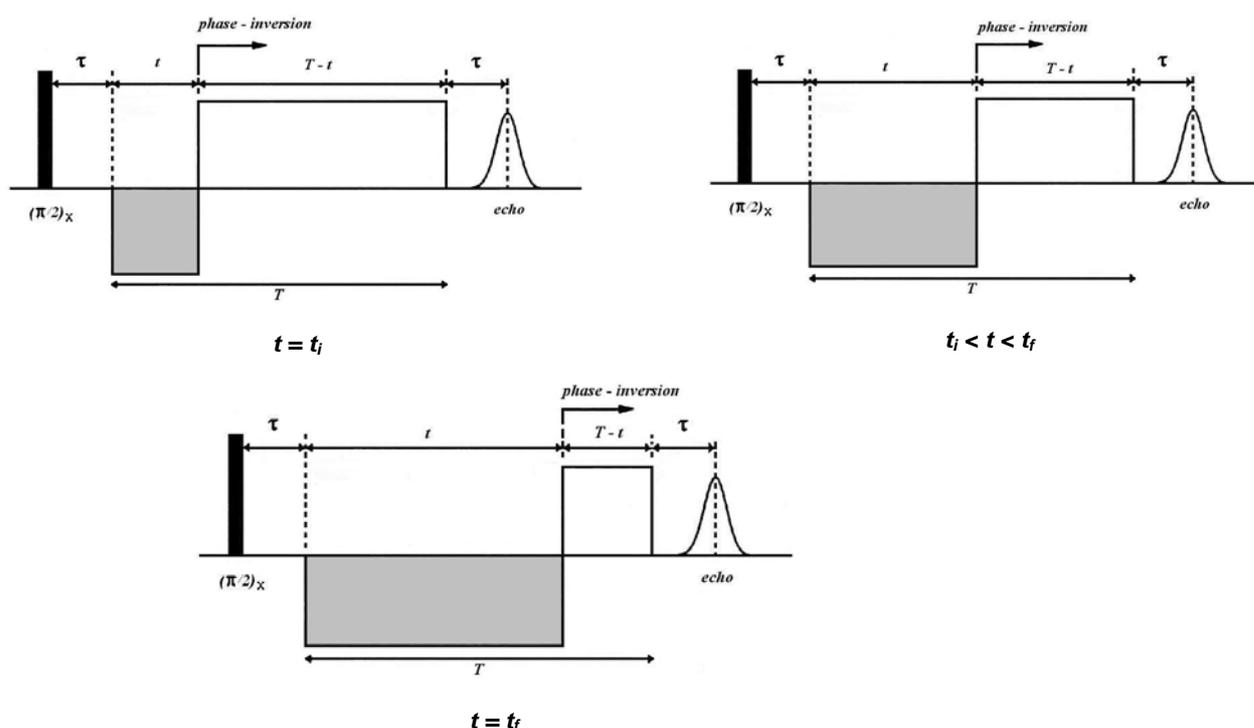

Figure 1. The PEANUT pulse sequence. Adapted from Reference [8].

Table 1

Chemical shifts and relative intensities observed in the ^{13}C MAS NMR spectrum of C_{60}
charged with 1kbar O_2 for 48h. Data from Reference [8].

Number of O_2/C_{60}	δ (from TMS)	Relative Intensity
0	143.7	1.00
1	144.4	0.70
2	145.1	0.65
3	145.8	0.60
4	146.5	0.40
5	147.2	0.20
6	147.9	0.05

Experimental

EPR measurements were carried out on a Bruker ESP-380 FT/CW X-band spectrometer. In the PEANUT experiment a 400 ns pulse was followed by a 2408 ns refocusing composed pulse. Further details of the EPR measurements are described elsewhere.[9] The C_{60} sample used in the EPR measurements was purchased from Southern Chemicals Co., with 99.5% purity.

Experimental details concerning the ^{13}C MAS NMR experiments can be found in the original work of Belahmer *et al.*[4] Briefly speaking, fullerene samples were prepared and purified by standard methods, annealed for 12 h at 240 °C under vacuum and kept in air at room temperature for one year. NMR experiments were performed in a Bruker CXP 200, at 50.3 MHz for the ^{13}C resonance.

Results and Discussion

As first noted by Myers et al.,[10] the exposure of C_{60} powder to O_2 at moderate pressures leads to the appearance of several new lines in the ^{13}C MAS NMR spectrum. These secondary lines are shifted downfield from the C_{60} main resonance peak (143.7 ppm from TMS), and are attributed to the Fermi-contact interaction of the paramagnetic oxygen molecules with the ^{13}C nuclear spins. Table 1 illustrates the chemical shifts and relative intensities of the seven peaks observed in the ^{13}C MAS NMR spectrum of C_{60} exposed to 1kbar of oxygen for 48 hours.

In ambient conditions, e.g., a non-treated sample, the fullerene-oxygen interaction is reflected in the ^{13}C MAS NMR spectrum as a low intensity peak (about 2.9% of the total intensity of the spectrum) at 144.4 ppm. This situation corresponds to the case of low charge of oxygen, namely one oxygen molecule per fullerene unit cell. It was noted that annealing of a C_{60} sample at 230 °C for 12h under vacuum reduces the intensity of the 144.4-ppm line. Accordingly to Belahmer *et al.*,[4] this result is in agreement with the hypothesis of intercalated oxygen instead of oxygen covalently bonded to the C_{60} molecules. These authors also noted that exposing the annealed sample to air at room temperature induced a new increase of the intensity of the δ 144.4 line, which indicates diffusion of O_2 into the system. Thus, the partially reversible contamination of C_{60} by molecular oxygen becomes clear.

Contamination of solid fullerene by oxygen corresponds to a situation where the intercalant interacts weakly with the host. The effects of oxygen intercalation at the fullerene lattice are also detectable by pulse EPR. Using the PEANUT pulse scheme, briefly described before, it was possible to discriminate paramagnetic species in the sample. In Figure 2 it is shown a stacked plot of the absolute valued Fourier transformed time data (a 2D-PEANUT spectrum). Cross-sections (nutation frequency selective EPR spectra) at 7.5 and 10.4 MHz give the single spectrum of each of the paramagnetic species.
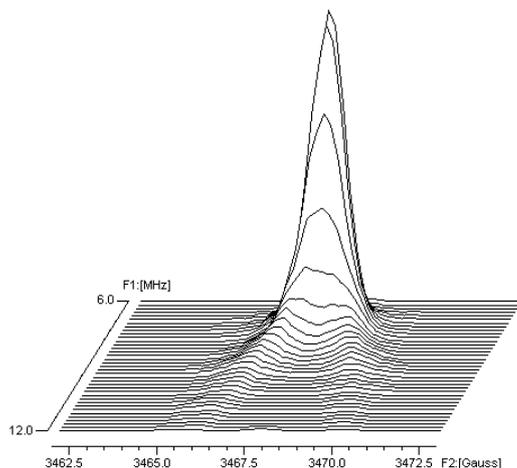
Figure 2. 2D-PEANUT stacked plot of the absolute valued FT data of C$_{60}$ powder sample. Details of spectral assignment are given in the text.

The 2D PEANUT spectra shown in Figure 2 allows a field-swept EPR spectrum to be spread into a second dimension, according to the transition moments of the individual EPR lines. This makes possible the separation of lines belonging to different sites and magnetic quantum numbers in the fullerene crystal lattice. The introduction of the nutation frequency ν_{TN} as a second dimension improves the resolution, since each transition has a characteristic nutation frequency, which depends on the magnitude of the magnetic moment μ. For example, the external magnetic field necessary to a $\pi/2$ turning angle for a triplet species is $\sqrt{2}$ smaller than the field required for a doublet species.

The ratio of the nutation frequencies measured in this PEANUT experiment is approximately $\sqrt{2}$, indicating that the higher nutation frequency species is a spin triplet with zero-field splitting (ZFS) of 0.25 mT. As briefly described in the Introduction, the EPR spectrum of solid C$_{60}$ shows low intensity lines flanking the main resonance. These signals have been attributed to dimmers formed by two spin doublet species present in solid fullerenes.[9] Using a point dipole approximation described in Ref. 9, the distance between the two interacting centres were evaluated as 16.7 Å. As the fullerene diameter is 7.1 Å, coupling most probably occurs between paramagnetic centres located at opposite sides of two adjacent C$_{60}$ molecules. This situation is in accordance with the intercalation of oxygen

molecules into the octahedral cavities of fullerene crystal lattice, as shown in Figure 3.
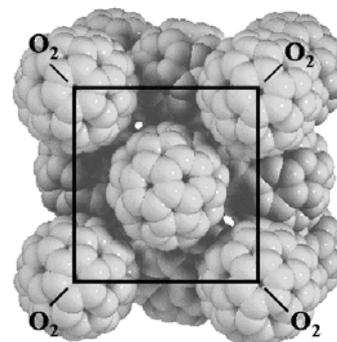

Figure 3. C$_{60}$ lattice showing the schematic representation of oxygen intercalation. Further details are given in the text. Some interactions are omitted for clarity.

The frame on Figure 3 represents de interaction between oxygen molecules belonging to adjacent fullerenes or between oxygen molecules located at the cube face diagonal. Interactions of oxygen molecules located at the cube diagonal are omitted for clarity. The latter interaction is observed only in the PEANUT experiment.

On the other hand, the ZFS of 0.25 mT measured by the PEANUT experiment corresponds to a distance of about 28 Å. In this case, interacting centres should be localised in fullerene molecules belonging to a face diagonal or to the cube diagonal of the fullerene *fcc* crystal lattice. It is worth of note that interaction between fullerene molecules located at the cube edge and at the centre of the cube face was not observed in this experiment. This suggests that, as pointed out in Ref. 11, electrostatic and packing hindrances precludes the formation of doublet species in these sites.

Conclusions

Independent ^{13}C MAS NMR measurements suggest weak and partially reversible interaction between oxygen and C$_{60}$, supporting the hypothesis of *fcc* octahedral voids occupation by oxygen molecules. However, this technique is unable to evaluate the distance between the interacting oxygen-containing sites. On the other hand, pulsed EPR is able to determine the distances between these centres, lightening the complementary

character of these resonance techniques. EPR data shows that the fullerene - oxygen interaction occurs even under normal conditions of temperature and pressure. As shown by the PEANUT experiment, oxygen molecules should be located at the face or cube diagonals of the fullerene crystal lattice. Thus, on studying fullerene materials or compounds it is important to realise that oxygen contamination is an unavoidable feature, inducing the formation of paramagnetic centres. In actually 'pure' fullerenes these centres should not be present. The novel PEANUT pulse sequence proved to be a deciding pulse technique to investigate paramagnetic centres in solid fullerene materials that may provide complementary information to that obtained by NMR spectroscopy.

Acknowledgements

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