High Resolution $^{13}C$ NMR study of oxygen intercalation in $C_{60}$

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Solid state high resolution $^{13}C$ NMR has been used to investigate the physical properties of pristine $C_{60}$ after intercalation with molar oxygen. By studying the dipolar and hyperfine interactions between Curie type paramagnetic oxygen molecules and $^{13}C$ nuclei we have shown that neither chemical bonding nor charge transfer results from the intercalation. The $O_2$ molecules diffuse inside the solid $C_{60}$ and occupy the octahedral sites of the fcc crystal lattice. The presence of oxygen does not affect the fast thermal reorientation of the nearest $C_{60}$ molecules. Using Magic Angle Spinning we were able to separate the dipolar and hyperfine contributions to $^{13}C$ NMR spectra, corresponding to buckyballs adjacent to various numbers of oxygen molecules.

I. INTRODUCTION

$C_{60}$ under its molecular or solid form, is an ideal system for $^{13}C$ NMR investigation. All carbons on the molecule are chemically equivalent, yielding an unique resonance at 143.6 ppm from the TMS reference, characteristic of an aromatic system [1]. Also, due to the Van der Waals nature of the solid, intermolecular interactions are very weak and the resonance in the solid is similar to that in solution [2]. Such a situation is particularly interesting as any change on the ball itself (substitution, addition) or any chemical intercalation in the fcc structure of the solid will be easily detected by $^{13}C$ NMR.

A simple situation is observed when the intercalant does not induce charge transfer with the host molecules. In this case the measured shift for the $^{13}C$ resonance is a chemical shift eventually corrected by contributions coming from the environmental disturbance. A typical case is $C_{60}$ intercalated with oxygen. As first shown by Assink et al [3], by submitting $C_{60}$ pr to a high pressure of oxygen, this species easily diffuses in the octahedral sites of the fcc crystal structure. Due to the paramagnetic nature of the molecule, the contact interaction between $^{13}C$ and oxygen orbitals produces a small shift whose amplitude is proportional to the magnetization (Curie law). This effect is additive and the shift corresponding to $C_{60}$ molecules, surrounded by $q$ ($6 \geq q \geq 2$) oxygens is $q$ times larger than the shift caused by one oxygen. Assink et al have also shown that the $^{13}C$ relaxation time for $C_{60}$ molecules surrounded by one or more oxygens is considerably decreased if compared with pure $C_{60}$ [4]. More recently, Belahmer et al have shown [5] that all these effects occur even if only ambient oxygen pressure conditions are imposed to the system.

In this paper we present a new study of the effect of oxygen. By comparing High-Resolution and static NMR spectra we were able to pick out the dipole-dipole interaction between the $^{13}C$ nuclear and $O_2$ magnetic moments.
This allowed us to calculate the $C_{60}-O_2$ intermolecular distance very accurately and to conclude that oxygen molecules carry the electronic spin $S = 1$ and occupy only the octahedral sites of the fcc lattice. No influence of the intercalated oxygen on the chemical and dynamical properties of $C_{60}$ has been observed. This conclusion was confirmed by the investigation of the dipolar contribution in the case of two surrounding oxygens, extracted from the sidebands envelope of the Magic Angle Spinning spectra.

II. EXPERIMENTAL

The $C_{60}$ powder has been obtained using a standard procedure yielding a 99.9% pure sample. The whole batch was kept in air and in the dark for a period of at least four months prior to experiment. In some cases a 9% $^{13}C$ enriched sample was used in order to improve thenal to noise ratio. $^{13}C$ NMR spectra of powdered highly crystalline samples were recorded on a Bruker CXP200 or ASX200 spectrometer working at 50.3 MHz. Magic angle spinning (MAS with a rotational frequency from 0.1 to 6kHz) was necessary to obtain high resolution and sensitivity. The chemical shifts are reported to the classical reference TMS.

Variable temperature (in the range 220 to 350K) with high resolution conditions was obtained using a cold or hot bearing gas flow.

III. RESULTS AND DISCUSSION

Figure 1 presents the spectrum obtained at room temperature and ambient air pressure with MAS (at 4 kHz) for the 9% $^{13}C$ enriched sample. In addition to the expected resonance at 143.6 ppm due to $C_{60}$ molecules in a perfect fcc environment, we observe five weak resonances whose positions are multiple of + 0.7 ppm from the main resonance. By reference to the work performed by Assink et al. \[3\] it is clear that these resonances correspond to the various cases of oxygen occupancy in the six octahedral sites around each $C_{60}$ molecule (Figure 2). Note that in our case we do not observe the sixth line which is probably too weak as we work at ambient air pressure. The first resonance close to the main line then corresponds to the case when one oxygen is adjacent to a $C_{60}$ molecule, the second peak corresponds to the two oxygen environment etc.

It must be noticed that the intensities of these lines rapidly decrease and scale as $I_1 : I_2 : I_3 : I_4 : I_5 = 1 : 0.04 : 0.007 : 0.005 : 0.001$. The ratio $I_0 : I_1 = 0.025$ obtained at the condition of fully relaxed pure $C_{60}$ spectrum with intensity $I_0$ with repetition time of 5min, gives the concentration of oxygen as $n = 2.5\%$ per $C_{60}$ molecule. Compare now the factor of the ratio of the first two
peaks, \( I_1 : I_2 = 1 : 0.04 \), with that which would be expected in the case when 2.5% of \( \text{O}_2 \) molecules were uniformly distributed over the sample. The later is provided by the probability of having two \( \text{O}_2 \) molecules located near the same buckyball sphere and is given by:

\[
I_1 : I_2 = 18n^2 = 1 : 0.01
\]

where factor 18 is the number of possible octahedral positions which can be joined with the given oxygen octahedral site \( \text{via} \) neighboring \( \text{C}_{60} \) molecules. Since this ratio is smaller than that measured experimentally we conclude that the equilibrium condition of the uniform oxygen distribution is not achieved and oxygen concentration diminishes from the surface of powder pieces to their center. Note however that in our case the oxygen distribution is much close to the uniform one than it was observed in the experiments of Assink [3] where the characteristic values of \( I_1 : I_2 \) were \( 1 : 0.4 \div 1 : 0.5 \) with approximately the same oxygen concentration and the exposition time was measured in hours.

From the \( ^{13}\text{C} \) NMR spectrum of oxygen doped fullerenes we argue that no charge transfer occurs from \( \text{O}_2 \) molecules to \( \text{C}_{60} \). All the spectrum properties are provided by the paramagnetic ground state of molecular oxygen, where two valence electrons form the triplet state with \( S = 1 \). The shift is attributed \( [3] \) to the isotropic hyperfine coupling, which presumably has the Fermi-contact type, of \( ^{13}\text{C} \) nuclei with the Curie type magnetic moments \( \mu_S \) of the neighbor oxygen molecules:

\[
\mu_S = (g\mu_B)^2S(S+1)B_0/3kT = 4\mu_B^2S(S+1)B_0/3kT
\]

(with \( g = 2 \)).

The hyperfine interaction, being strongly dependent on the distance between \( \mu_S \) and \( ^{13}\text{C} \) nuclei, is effectively averaged by the fast thermal reorientation of those and therefore can be described by the hyperfine coupling constant \( A_{\text{eff}} \) taken as an average of the \( \mu_S - ^{13}\text{C} \) hyperfine interaction over the neighbor to the oxygen buckyball re. The isotropic shift, \( \sigma_{\text{iso}} \), is then inversely proportional to the temperature and to the number of oxygens \( q \) (with a maximum of 6) neighbors of a given \( \text{C}_{60} \) molecule:

\[
\sigma_{\text{iso}} = q \left( \frac{A_{\text{eff}}}{\hbar} \right) \frac{g\mu_B S(S+1)}{3kT\gamma_I} \tag{1}
\]

where \( \gamma_I \) is a nuclear magnetogryic ratio. The inverse temperature behavior of \( \sigma_{\text{iso}} \) observed experimentally \( [3] \) confirms the hyperfine rather than charge transfer origin of \( \sigma_{\text{iso}} \).

By studying the anisotropic spectrum obtained with no MAS we show that the intercalated oxygen molecules do have the spin \( S = 1 \) and therefore no electrons came from \( \text{O}_2 \) to \( \text{C}_{60} \). Figure 3(a) presents the static spectrum obtained with such a condition on the same sample as above. A superposition of two components is observed:

i) a symmetric line centered at 143.6 ppm, with a width of roughly 3 ppm, which correspond to \( \text{C}_{60} \) molecules not adjacent to any oxygen molecule;

ii) an anisotropic spectrum which expands from 125 ppm to 175 ppm and corresponds to \( \text{C}_{60} \) molecules aju-
cent to only one oxygen. Taking into account the intensities of the various isotropic resonances (Fig.1), we expect that the anisotropic spectrum corresponding to two or more oxygens should be extremely weak. Note also that at very low spinning frequency (MAS) of the sample (Fig.3(b)), all the observed spinning side bands correspond to the isotropic resonance of the "one oxygen" case, and their envelope reproduces the static spectrum of Figure 3(a).

The origin of the anisotropic spectrum is the IS dipolar interaction between the oxygen and $^{13}$C magnetic moments. Two limiting situations have to be considered: the $O_2$-$^{13}$C vector $r_i$, can be either parallel or perpendicular to the external magnetic field. In first case the shift $\sigma_\parallel$ is paramagnetic, while in the second one the shift $\sigma_\perp$ is diamagnetic and twice as smaller in magnitude as $\sigma_\parallel$. The powder spectrum is provided by the all intermediate positions of the vector $r_i$.

On a quantitative basis, the IS dipolar interaction results in the traceless uniaxial NMR shift tensor $\sigma_{ij}$:

$$\sigma_{ij} = \mu_S \left( \frac{3 r_i r_j}{r^3} - \frac{\delta_{ij}}{r^3} \right) \frac{1}{B_0} \quad (2)$$

The fast thermal reorientation of $C_{60}$ molecule leads to the effective averaging of (2) over all the possible locations of $^{13}$C, i.e. over the surface of the neighboring $C_{60}$ molecule. Calculating this average finally we obtain:

$$\overline{\sigma}_{ij}(l) = \frac{4\mu_B}{3kT}S(S+1) \left( \frac{l_i l_j}{l^3} - \frac{\delta_{ij}}{l^3} \right) \quad (3)$$

Where $l_i$ is the vector joining the centers of the $O_2$ and $C_{60}$ molecules. The static NMR spectrum is determined by the powder pattern of the tensor and has the shape shown on Figure 3. The principal values of $\boldsymbol{\sigma}_{ij}$, which corresponds to $\sigma_\perp$ and $\sigma_\parallel$ give the width of the spectrum: $\Delta \sigma = \sigma_\parallel - \sigma_\perp$. From (3) we have:

$$\sigma_\perp = -S(S+1) \frac{4\mu_B^2}{3kT l^3} \quad \sigma_\parallel = 2S(S+1) \frac{4\mu_B^2}{3kT l^3} \quad \Delta \sigma = \frac{4}{kT} S(S+1) \frac{\mu_B^2}{l^3} \quad (4)$$

Figure 4 shows that the inverse temperature behavior for $\Delta \sigma$ does take place at least in the range 240-340 K. Note the clearly observed drop of $\Delta \sigma$ at a temperature close to the first order transition temperature $T_c = 260$ K.

From the expression above, with $\Delta \sigma = 48$ ppm at $T = 300K$, assuming $S = 1$, one obtain $l = 7\AA$ (with 4% accuracy) which exactly corresponds to the distance from the buckyball sphere center to the nearest octahedral position of oxygen. We then conclude that:

(i) oxygen molecules stay exact in the middle of the octahedral site of fcc lattice, no tetrahedral positions are populated by oxygen;

(ii) the oxygen molecules carry the electronic spin $S = 1$ and therefore neither charge transfer nor chemical bonding resulting from oxygen occurs in the system.
(iii) the width of the one-oxygen static NMR spectrum is provided by the dipolar $^{13}\text{C} - O_2$ interaction, rather then the buckyball rotation hindrance by the intercalated oxygen as it was suggested by [4]. The intercalated oxygen has no influence on the $C_{60}$ thermal reorientations, at least in NMR time scale $2 \cdot 10^{-8}$s.

With $l$ being half of the fcc lattice constant, we can imagine that the small drop of $\Delta \bar{\sigma}$ at 260 K could be due to the experimentally observed contraction of the lattice at the transition [4][5]. Nevertheless this contraction induces a variation of the lattice parameter smaller than 0.2%, which cannot account for the measured 16% drop of $\Delta \bar{\sigma}$ at 260K. We suggest that the large drop of $\Delta \bar{\sigma}$ could be attributed to the partial blocking of the movement of the nearest to the oxygen $C_{60}$ molecules after the transition.

Now we show that the two-oxygen NMR spectrum is also provided by the spin paramagnetism of oxygen molecules and confirms the given above conclusions about the oxygen state in $C_{60}$. Technically this is more delicate to study. The isotropic part of the spectrum is easy to detect at 1.4 ppm from the main line (Figure 1), which is twice the value for the one-oxygen case. This corresponds to the doubling of the effective hyperfine interaction, according to (1) (with $q = 2$). The anisotropic spectrum cannot be obtained directly as it was in the one-oxygen case. The main reason is the very weak signal to noise ratio as a result of the small number of $C_{60}$ molecules surrounded by two oxygens and the increasing width of the anisotropic spectrum. The only way to get some information on the shape of the spectrum is to record the High Resolution spectrum with enough spinning side bands to be able to study their envelope. After this, assuming that the envelope has a similar form than static spectrum [10] we can compare it to the theoretical predictions.

The calculation of the shape of the two-oxygen static NMR spectrum uses the same assumptions as above: the $C_{60}$ balls are supposed to rotate freely at room temperature and the molecular oxygen occupies the octahedral sites only. Then we have to consider two cases: two oxygens are located along the same axis going through the $C_{60}$ center, e.g. A and B on Figure 2 (diametral arrangement) or they are located on the perpendicular axis: A and C, D, E or F on Figure 2 (rectangular arrangement). Considering a given octahedral oxygen site, surrounded by six $C_{60}$ molecules, we find that there exist twelve neighbor octahedral sites which correspond to the rectangular oxygens arrangement and six corresponding to the diametral case. Therefore the rectangular location is twice as probable as the diametral one.

Formally, the NMR shift tensor results from the contributions of the dipolar NMR shift tensors from both oxygens, surrounding $C_{60}$ molecule:

$$\sigma_{ij}^{2ox} (b_1 \cdot l_2) = \sigma_{ij}^{ox}(l_1) + \sigma_{ij}^{ox}(l_2)\quad (5)$$

Here $l_1$, $l_2$ are the unit vectors directed from the center of $C_{60}$ to the oxygen positions (either diametral or...
rectangular arrangement), \( \sigma_{ij}(l) \) is the dipolar shift tensor given by (3). Therefore the relative location of \( O_2 \) molecules with respect to \( C_{60} \) is important and the intensity of the resulting lineshape is the sum of two contributions:

\[
I^{2ox} = 6 \cdot I^\pi (\sigma) + 12 \cdot I^{\pi/2} (\sigma)
\]

The lineshapes \( I^\pi (\sigma), I^{\pi/2} (\sigma) \), for the diametral and rectangular oxygen arrangements correspond to the powder patterns of the tensor (3) with \( l_1 \cdot l_2 = \pi \) and \( l_1 \cdot l_2 = \pi/2 \) respectively, factor 6 and 12 being the above mentioned population ratios for the diametral and rectangular oxygen locations. Both oxygen arrangements give powder lineshapes having uniaxial tensors \( \sigma^{2ox}_{ij} (\pi/2) \), with the following principal values:

for diametral location:

\[
\sigma^{2ox}_{\perp} (\pi) = -\frac{16}{3kT} \mu_B^2 \quad \sigma^{2ox}_{\parallel} (\pi) = 2 \cdot \frac{16}{3kT} \mu_B^2 \quad \Delta \sigma^{2ox} (\pi) = \frac{16}{kT} \mu_B^2 \frac{B^2}{l^3} \quad (7a)
\]

for rectangular location:

\[
\sigma^{2ox}_{\perp} \left( \frac{\pi}{2} \right) = \frac{8}{3kT} \mu_B^2 \quad \sigma^{2ox}_{\parallel} \left( \frac{\pi}{2} \right) = -2 \cdot \frac{8}{3kT} \mu_B^2 \frac{B^2}{l^3} \quad \Delta \sigma^{2ox} \left( \frac{\pi}{2} \right) = \frac{8}{kT} \mu_B^2 \frac{B^2}{l^3} \quad (7b)
\]

The resulting NMR spectrum extends over more than 90 ppm and presents two well defined maxima as shown on Figure 5. We have also presented the experimental amplitudes of the spinning side bands (the accuracy is not better than 30% in this case) as obtained after a long accumulation and using a low spinning frequency (400 Hz). Taking into account the extent of the spectrum and the poor signal over noise ratio we consider that there is a reasonable agreement with the predicted spectrum.

IV. CONCLUSION

Using static and high resolution \(^{13}\text{C}\) NMR, we have shown that presence of oxygen in solid \( C_{60} \) in equilibrium with ambient air pressure can be easily detected. The molecular oxygen is located exactly in the middle of the octahedral sites of the fcc crystal lattice and has the electronic spin \( S = 1 \), corresponded to the paramagnetic moment of \( O_2 \) molecule. Therefore no charge transfer results from the oxygen intercalation. The case of one oxygen per \( C_{60} \) can be analyzed quite accurately by separate studying of the dipolar- and contact hyperfine contributions to the NMR spectra. We conclude that the presence of molecular oxygen does not affect significantly either the chemical or the dynamical properties of solid \( C_{60} \). Two-oxygen NMR spectra confirm the given conclusions.
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FIG. 1. $^{13}$C NMR spectrum of $C_{60}$ powder contaminated with oxygen at ambient conditions. The intensity of the main line at 143.6 ppm is artificially decreased by reference to the other lines, as the recycling time is very short (1.5 s) compared to its relaxation time (at least 100 s).

FIG. 2. Schematic representation of the six octahedral sites (noted A, B, C, D, E and F) of the fcc lattice around $C_{60}$ molecule.

FIG. 3. $^{13}$C NMR spectra of the sample of Figure 1. a) Static spectrum obtained with no MAS showing the superposition of the two lines. b) Same conditions, but obtained with a low frequency MAS of 116 Hz.

FIG. 4. Variation of $\Delta \sigma$ defined as the distance in ppm between the two sides of the anisotropic spectrum such as presented in Figure 3. versus the inverse temperature, showing the linear dependence and the slight drop close to $T = 260$ K.

FIG. 5. Amplitudes of the spinning side bands corresponding to the two oxygens per $C_{60}$ case. We compare the experimental data with the predictions of theory (full line). The two component spectra (dashed lines) correspond to the two situations described in the text.