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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 molecular 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 fullerenes adjacent to various numbers of oxygen molecules.

I. INTRODUCTION

C_{60} in its molecular or solid form is an ideal system for ^{13}C NMR investigation. All carbons on the molecule are chemically equivalent, yielding a unique resonance at 143.6 ppm from the tetramethylsilane (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.*[3,4] by submitting C_{60} powder to air and to a high pressure of oxygen, the O_2 molecules easily diffuse in the octahedral sites of the fcc structure. Due to the paramagnetic nature of the molecule, the contact interaction between ^{13}C and oxygen orbitals produces a small shift, the amplitude of which is proportional to the magnetization (Curie law). This effect is additive and the shift corresponding to C_{60} molecules surrounded by q $(6 \geqslant q \geqslant 2)$ oxygen molecules is q times larger than the shift caused by one oxygen molecule. Assink *et al.* have also shown that the ^{13}C relaxation time for C_{60} molecules surrounded by one or more oxygen molecules is considerably decreased if compared with pure C_{60}.[3,4] More recently, Belahmer *et al.* have shown[5] that all these effects occur even if only ambient oxygen pressure conditions are imposed on the system.

In this paper we present a 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 oxygen molecules, extracted from the sideband envelope of the magic angle spinning spectra.

II. EXPERIMENT

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 the signal-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 6 kHz) was necessary to obtain high resolution and sensitivity. The chemical shifts are reported to the classical reference TMS. Variable temperature (in the range 220–350 K) 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, the positions of which are multiples of +0.7 ppm from the main resonance. By reference to the work performed by Assink *et al.*[3,4]

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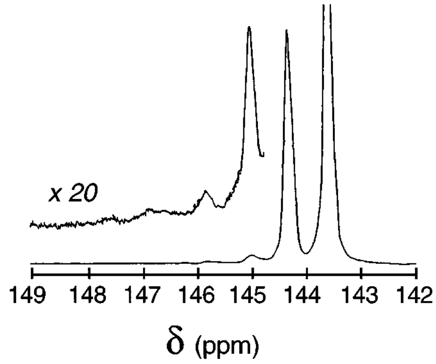

FIG. 1. ^{13}C NMR spectrum of C_{60} powder contaminated with oxygen at ambient conditions. The intensity of the main line at 143.6 ppm is artificially decreased by reference to the other lines, as the recycling time is very short (1.5 s) compared to its relaxation time (at least 100 s).

it is clear that these resonances correspond to the various cases of oxygen occupancy in the six octahedral sites around each C_{60} molecule (Fig. 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 with intensity I_1 close to the main line then corresponds to the case when one oxygen molecule is adjacent to a C_{60} molecule, the second peak I_2 corresponds to the two-oxygen-molecule 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 of the oxygen-free to the one-oxygen-molecule peaks' intensities, $I_0:I_1 = 1:0.025$, where both I_0 and I_1 were obtained at the condition of the fully relaxed pure C_{60} spectrum with repetition time of 5 min, gives the concentration of oxygen as $n=(I_1:I_0)/6=0.4\%$ per C_{60} molecule, providing that six C_{60} molecules surround the octahedral oxygen locations. 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 $n=0.4\%$ of O_2 molecules were uniformly distributed over the sample. The latter is provided by the probability of having two O_2 molecules located near the same fullerene sphere and is given by $I_1:I_2=18n^2 = 1:(3\times10^{-4})$, where the factor 18 is the number of possible octahedral positions that can be joined with the given oxygen octahedral site via neighboring C_{60} molecules. Since this ratio is substantially 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.

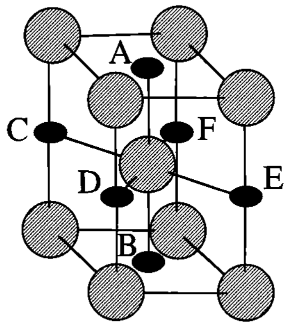

FIG. 2. Schematic representation of the six octahedral sites (noted *A*, *B*, *C*, *D*, *E*, and *F*) of the fcc lattice around the C_{60} molecule.

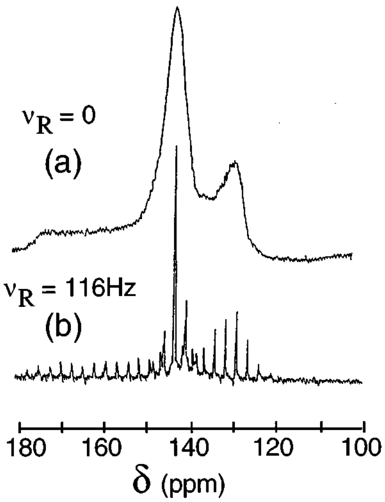

FIG. 3. ^{13}C NMR spectra of the sample of Fig. 1. (a) Static spectrum obtained with no MAS showing the superposition of the two lines. (b) Same conditions, but obtained with a low-frequency MAS of 116 Hz.

From the ^{13}C NMR spectrum of oxygen-doped fullerenes we argue that no charge transfer occurs from O_2 molecules to C_{60}. All the spectral 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[4] to the isotropic hyperfine coupling, which presumably has the Fermi-contact type of ^{13}C nuclei with the Curie-type magnetic moments μ_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 μ_S and ^{13}C nuclei, is effectively averaged by the fast thermal reorientation of those and therefore can be described by the hyperfine coupling constant A_{eff} taken as an average of the μ_S-^{13}C hyperfine interaction over the neighbor to the oxygen fullerene sphere. The isotropic shift σ_{iso} is then inversely proportional to the temperature and to the number of oxygen molecules q (with a maximum of six) that are neighbors of a given C_{60} molecule:

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

where γ_I is a nuclear magnetogyric ratio. The inverse temperature behavior of σ_{iso} observed experimentally[4,9] confirms the hyperfine rather than charge-transfer origin of σ_{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 O_2 to 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 C_{60} molecules not adjacent to any oxygen molecule; and (ii) an anisotropic spectrum that expands from 125 ppm to 175 ppm and corresponds to C_{60} molecules adjacent to only one oxygen molecule. Taking into account the intensities of the various isotropic resonances (Fig. 1), we expect that the anisotropic spectrum corresponding to two or more oxygen molecules should be extremely weak. Note also that at very low spinning frequency (MAS) of the sample [Fig. 3(b)], all the observed spinning sidebands correspond to the isotropic resonance of the "one-oxygen-molecule" case, and their envelope reproduces the static spectrum of Fig. 3(a).[6]

The origin of the anisotropic spectrum is the dipolar interaction between the oxygen and ^{13}C magnetic moments. This interaction results in the traceless uniaxial NMR shift tensor σ_{ij},

$$\sigma_{ij}=\mu_S\left(3\frac{r_ir_j}{r^5}-\frac{\delta_{ij}}{r^3}\right)\frac{1}{B_0}, \tag{2}$$

where r_i is the O_2-^{13}C vector.

The fast thermal reorientation of the 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. Calculation of this average finally results in the effective NMR shift tensor,

$$\sigma'_{ij}(\boldsymbol{l})=\frac{4\mu_B}{3kT}S(S+1)\left(3\frac{l_il_j}{l^5}-\frac{\delta_{ij}}{l^3}\right), \tag{3}$$

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

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

$$\Delta\sigma'=\frac{4}{kT}S(S+1)\frac{\mu_B^2}{l^3}. \tag{4}$$

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.[7,8]

From the expression above, with $\Delta\sigma'=48$ ppm at $T=300$ K, assuming $S=1$, one obtains $l=7$ Å (with 4% accuracy), which exactly corresponds to the distance from the fullerene sphere center to the nearest octahedral position of oxygen. We then conclude that (i) oxygen molecules stay exactly in the middle of the octahedral site of an fcc lattice, while 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; and (iii) the line shape of the one-oxygen-molecule static NMR spectrum is provided by the dipolar ^{13}C-O_2 interaction, rather than the fullerene rotation hindrance by the intercalated oxygen, as was suggested by Ref. 5. The intercalated oxygen has no influence on the C_{60} thermal reorientations, at least in the NMR time scale 2×10^{-8} s.

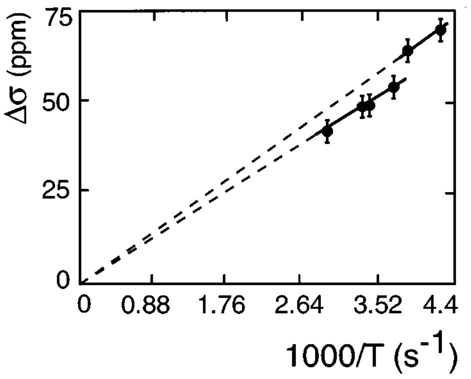

FIG. 4. Variation of $\Delta\sigma$ defined as the distance in ppm between the two sides of the anisotropic spectrum, such as presented in Fig. 3, versus the inverse temperature, showing the linear dependence and the slight drop close to $T=260$ K.

With l being half of the fcc lattice constant, we can imagine that the small drop of $\Delta\sigma'$ at 260 K could be due to the experimentally observed contraction of the lattice at the transition.[7,8] Nevertheless, this contraction induces a variation of the lattice parameter smaller than 0.2%, which cannot account for the measured 16% drop of $\Delta\sigma'$ at 260 K. We suggest that the large drop of $\Delta\sigma'$ 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-molecule NMR spectrum is also provided by the spin paramagnetism of oxygen molecules and confirms the above conclusions about the oxygen state in C_{60}. Technically this case is more delicate to study. The isotropic part of the spectrum is easy to detect at 1.4 ppm from the main line (Fig. 1), which is twice the value for the one-oxygen-molecule 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-molecule 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 oxygen molecules 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 sidebands to be able to study their envelope. After this, assuming that the envelope has a form similar to static spectrum,[10] we can compare it to the theoretical predictions.

The calculation of the shape of the two-oxygen-molecule static NMR spectrum uses the same assumptions as above: the fullerenes 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 oxygen molecules are located along the same axis going through the C_{60} center, e.g., A and B in Fig. 2 (diametral arrangement), or they are located on the perpendicular axis, as A and C, D, E, or F in Fig. 2 (rectangular arrangement). Considering a given octahedral oxygen site surrounded by six C_{60} molecules, we find that there exist 12 neighbor octahedral sites that correspond to the rectangular oxygen-molecule 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 oxygen moleucles surrounding the C_{60} molecule:

$$\sigma_{ij}^{2\text{ox}}(\boldsymbol{l}_1\times\boldsymbol{l}_2)=\sigma'_{ij}(\boldsymbol{l}_1)+\sigma'_{ij}(\boldsymbol{l}_2). \tag{5}$$

Here $\boldsymbol{l}_1,\boldsymbol{l}_2$ are the unit vectors directed from the center of C_{60} to the oxygen positions (either diametral or rectangular arrangement); $\sigma'_{ij}(\boldsymbol{l})$ 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 line shape is the sum of two contributions:

$$I^{2\text{ox}}=6\times I^{\pi}(\sigma)+12\times I^{\pi/2}(\sigma). \tag{6}$$

The line shapes $I^{\pi}(\sigma),I^{\pi/2}(\sigma)$ for the diametral and rectangular oxygen arrangements correspond to the powder patterns of the tensor (3) with $\boldsymbol{l}_1\times\boldsymbol{l}_2=\pi$ and $\boldsymbol{l}_1\times\boldsymbol{l}_2=\pi/2$, respectively, factors 6 and 12 being the above-mentioned population ratios for the diametral and rectangular oxygen locations. Both oxygen arrangements give powder line shapes having uniaxial tensors $\sigma_{ij}^{2\text{ox}}(\pi)$ $\sigma_{ij}^{2\ \text{ox}}(\pi/2)$,with the following principal values:

$$\sigma_{\perp}^{2\text{ox}}(\pi)=-\frac{16}{3kT}\frac{\mu_B^2}{l^3},\quad \sigma_{\parallel}^{2\text{ox}}(\pi)=2\frac{16}{3kT}\frac{\mu_B^2}{l^3},$$

$$\Delta\sigma^{2\ \text{ox}}(\pi)=\frac{16}{kT}\frac{\mu_B^2}{l^3}, \tag{7a}$$

for diametral location,

$$\sigma_{\perp}^{2\text{ox}}\left(\frac{\pi}{2}\right)=\frac{8}{3kT}\frac{\mu_B^2}{l^3},\quad \sigma_{\parallel}^{2\text{ox}}\left(\frac{\pi}{2}\right)=-2\frac{8}{3kT}\frac{\mu_B^2}{l^3},$$

$$\Delta\sigma^{2\text{ox}}\left(\frac{\pi}{2}\right)=\frac{8}{kT}\frac{\mu_B^2}{l^3}, \tag{7b}$$

for rectangular location.

The resulting NMR spectrum extends over more than 90 ppm and presents two well-defined maxima as shown in Fig. 5. We have also presented the experimental amplitudes of the spinning sidebands (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.

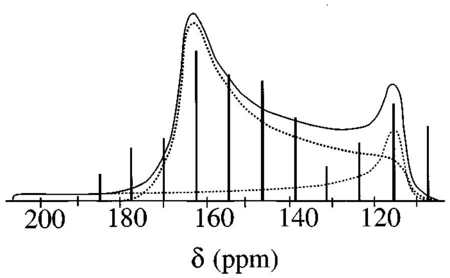

FIG. 5. Amplitudes of the spinning sidebands corresponding to the two oxygen molecules per C_{60} case. We compare the experimental data with the predictions of theory (full line). The two component spectra (dashed lines) correspond to the two situations described in the text.

IV. CONCLUSION

Using static and high-resolution ^{13}C NMR, we have shown that the 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 $S=1$, corresponding to the paramagnetic moment of an O_2 molecule. Therefore no charge transfer results from the oxygen intercalation. The case of one oxygen molecule per C_{60} molecule 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-molecule NMR spectra confirm the given conclusions.

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