Intercalation of O_2 in solid C_{60} and molecular-rotation hindrance

Z. Belahmer, P. Bernier, L. Firlej, J. M. Lambert, and M. Ribet

Groupe de Dynamique des Phases Condensées, Université de Montpellier II, 34095 Montpellier CEDEX 05, France

We present ^{13}C NMR experiments performed on pure C_{60} crystalline powders. High resolution in the solid state on a very pure sample allows us to measure an extremely narrow (1.8-Hz linewidth) resonance at 143.6 ppm characteristic of the rotating molecule. The intercalation of O_2 molecules in the fcc structure induces an additional resonance (at 144.3 ppm) whose intensity is directly related to the oxygen content. At room temperature the O_2 intercalation is partially reversible. By analysis of the ^{13}C resonance shape of this additional resonance we characterize the hindrance in the C_{60} rotation introduced by the intercalated species.

I. INTRODUCTION

Solids made of C_{60} molecules are among the most fascinating materials. When they crystallize in the fcc lattice the C_{60} molecules occupy only 66% of the apparent volume, leaving voids with octahedral symmetry of a dimension large enough to accommodate almost any element of the Periodic Table.[1] This situation has been exploited to produce intercalation compounds among which superconductors have been identified.[2] These compounds are obtained after heat treatment, usually at a temperature higher than 200 °C. More recently it has been shown that molecular oxygen readily and spontaneously intercalates in solid C_{60}.[3] This process is efficient even at room temperature and, on the contrary, any thermal treatment supposed to increase the molecular diffusion rate in the material will also induce irreversible chemical reactions.

Kept in standard conditions (room temperature and ambient pressure) the pure C_{60} powder absorbs a few percent of molecular oxygen, as shown by Assink *et al.* using ^{13}C NMR.[3] The usual resonance at 143.6 ppm [from tetramethylsilane (TMS)] associated with the carbon sites of the molecule in the fcc lattice presents a satellite line 0.7-ppm downfield shifted. This shift is associated with the weak paramagnetism on the O_2 molecule, which also induces a drastic increase of the ^{13}C relaxation rate. Depending on the number of surrounding O_2 molecules to a given C_{60} molecule, Assink *et al.* observe up to six additional lines, downfield shifted and equally spaced by 0.7 ppm. This intercalation process appears to be partially reversible.

In this paper we present a ^{13}C NMR study, using high resolution in the solid state, of the effects of oxygen intercalation on the dynamical characteristics of C_{60} molecules.

II. EXPERIMENT

Pure C_{60} powder has been obtained using standard procedures, after a chromatographic treatment of the fullerene mixture derived from carbon soot.[4] A purity of 99.5% could be achieved, as determined by high-pressure liquid chromatography (HPLC), after heat treatment at 240 °C during 12 h under vacuum. The samples, prepared in January 1992, were kept in air at room temperature from that time. All the NMR experiments have been made after at least four months of air exposure. These measurements have been performed with a Bruker CXP 200 NMR spectrometer working at 50.3 MHz for the ^{13}C resonance. A standard $\pi/2$ pulse has been used to generate the NMR signal, while magic-angle spinning (MAS) at various rates (from 0.3 to 2 KHz) was needed to achieve high resolution. Relaxation time T_1 has been measured using the usual $\pi - \pi/2$ inversion-recovery sequence.

III. RESULTS AND DISCUSSION

Figure 1 presents the ^{13}C NMR spectrum obtained at room temperature on a pure C_{60} powder whose good crystallinity and chemical quality has been checked by x-ray diffraction (XRD) and differential scanning calorimetry (DSC) and compared with published data.[5] A spectrum composed of two lines is observed. The intense line is associated with the freely rotating C_{60} molecules while the weak one concerns this part of the sample which is intercalated with oxygen, as suggested by Assink *et al.*[3]

The intense line (A), at a position 143.6 ppm (from TMS) referenced to the adamantane signal position, is extremely narrow (~ 0.036 ppm $= 1.8$ Hz). The small observed width has to be associated with the good crystallinity of the system. In effect it has been shown previously on organic materials that any significant decrease of crystallinity (by structural defects or by the size of the crystallites) results in a drastic increase of the residual width observed with high resolution.[6] By comparison with the case of pure diamond, we estimate that the size of C_{60} crystallites in our samples is of the order of a few thousand Å, consistent with a coherence length by XRD of the same order of magnitude. Finally, we have to note that the accuracy on the resonance position is mainly that of the reference (~ 0.1 ppm) and in the following only relative positions will be discussed.

The line at 143.6 ppm is the isotropic part of the static

symmetric spectrum, of width ~ 5 ppm, characteristic of the C_{60} rotational movement (at the origin of the motional narrowing of the resonance) observed at room temperature.[7] The small extent of the spectrum has to be compared with the large value of the chemical shift anisotropy ($\Delta\sigma \sim 220$ ppm) measured for the same system at low temperature, when the molecules are almost frozen.[8] The relaxation time T_1 strongly depends on the purity of the system and varies from ~ 30 to 150 s.[9] In the present case the measured $T_1 = 60$ s indicating that the bulk material is of reasonably good purity.

The weak resonance line (B) at 144.3 ppm has to be associated with C_{60} molecules having one O_2 molecule in one of the six surrounding octahedral sites, as proposed by Assink et al.[3] Without any preliminary treatment of the sample, this line represents 2.9% of the total intensity. If we suppose that there is only one O_2 molecule per C_{60}, such a number represents a diffusion of oxygen in the volume of the powder grains over a distance which is $\sim 5\%$ of the particle radius. No information exists at the moment on the kinetics of this diffusion process. Nevertheless, we have noted that very fresh samples do not usually present the resonance (B), which appears only after times of the order of days at ambient atmosphere. Assink et al. have interpreted the position of the resonance (B)

in terms of paramagnetic (Fermi contact) shift associated with the weak paramagnetism of molecular oxygen. Let us suggest that we cannot totally eliminate the possibility of having even a small charge transfer between oxygen and the C_{60} molecules, with a corresponding shift of the resonance. Such a shift is expected to be very small as 60 equivalent carbons have to share the transferred electronic charge, supposed to be much less than one electron.

We have noted [Fig. 2(a)] that the intensity of the resonance (B) decreases after the sample has been annealed (230 °C for 12 h) under vacuum ($< 10^{-5}$ Torr), in agreement with the hypothesis of the existence of intercalated oxygen instead of oxygen covalently bonded to the C_{60} molecules. In addition a further stay of the same sample in air at room temperature induced a new increase of the intensity of this resonance, indicating that oxygen is again diffusing in the system [Fig. 2(b)]. This process can be repeated showing that intercalation of oxygen in solid C_{60} is at least partly reversible.

The relaxation time T_1 is also strongly affected by the presence of oxygen. The T_1 value for resonance (B) is 0.22 s at room temperature, to be compared with 60 s for resonance (A). This large difference is due to a significant difference in the dynamical characteristics of molecules contributing to resonances (A) and (B). We also note that from 345 K down to 220 K T_1 presents a monotonic and weak decrease (from 0.22 to 0.15 s, respectively) without any sharp inflection as observed in the case of pure C_{60} around 258 K and due to the orientational order phase transition.[10] One way to understand the absence of transition and the short T_1 value of resonance (B) is to suggest that molecules surrounded by oxygen are no longer free to rotate. This hypothesis can be checked by looking
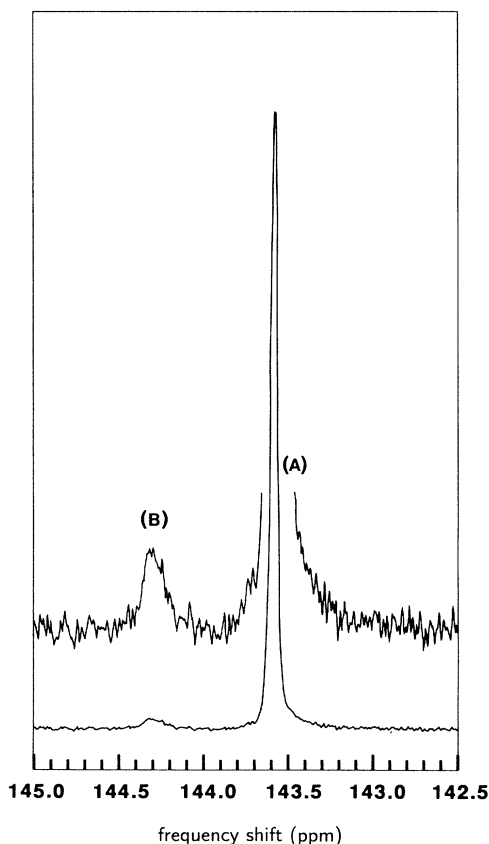

FIG. 1. ^{13}C high-resolution NMR spectrum of pure C_{60} at room temperature shown on two different vertical scales, showing one intense (A) and one weak (B) resonance.
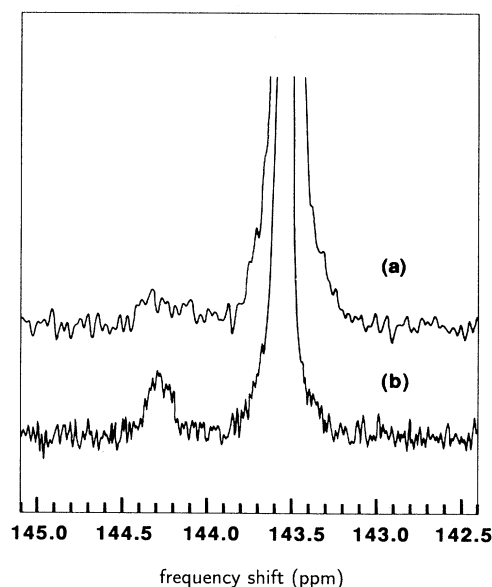

FIG. 2. Evolution of the ^{13}C NMR spectrum of pure C_{60} in contact with air: (a) after annealing at 230 °C for 12 h under vacuum ($< 10^{-5}$ Torr) and (b) same sample after annealing and exposure to air for 12 h.

at the resonance without the high-resolution conditions and observing if the C_{60} motional narrowing is existing for the resonance (B) as it is for the (A) one. Nevertheless, taking into account its small intensity it is impossible to observe the resonance (B) without high-resolution conditions. One solution consists of observing the high-resolution spectrum obtained with a sample spinning at a sufficiently small frequency (of the order of a few hundred Hz). In this case the chemical shift anisotropy will appear through the envelope of the whole spectrum composed of the isotropic line and all the spinning sidebands [Fig. 3(a)]. Such spectra are shown in Fig. 3(b) for the resonance (A) and Fig. 3(c) for the resonance (B). From these data and using a method developed by Herzfeld and Berger,[11] we can estimate the tensor components of the chemical shift anisotropy $\sigma_{11}=113\pm2$, $\sigma_{22}=156\pm3$, and $\sigma_{33}=163\pm2$ ppm. Then the extent of chemical shift an-

isotropy, of the order of 50 ppm, is at least ten times larger than the motionally narrowed resonance of pure C_{60} indicating a significant hindrance of the rotation of the molecules surrounded by oxygen. On the other hand, this anisotropy extent is three times smaller than the one measured for the frozen C_{60} molecules. This shows that the blocking of the C_{60} movement by the presence of oxygen is not total and some reorientation is still possible. This conlcusion favors the idea that there is a small charge transfer between the O_2 and C_{60} species which tends to impose preferential orientations of the molecules, limiting their degree of freedom.

IV. CONCLUSION

In this study we have shown that the oxygen intercalation in solid C_{60} has a profound influence on the dynami-
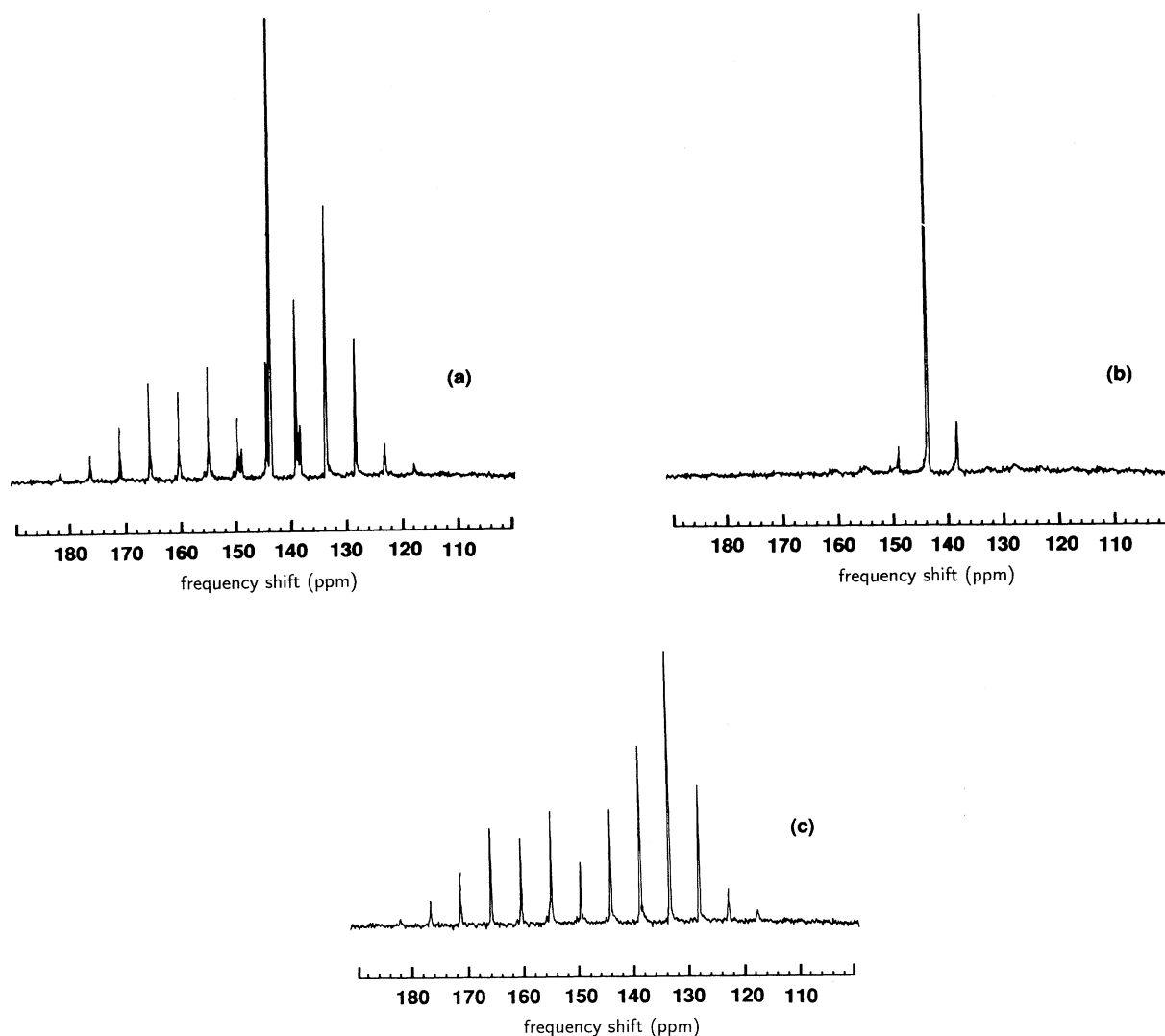

FIG. 3. (a) ^{13}C NMR spectrum of sample used for Fig. 1 obtained with a low MAS frequency $\nu_R=265$ Hz, (b) isotropic part and spinning sidebands for resonance (A), and (c) isotropic part and spinning sidebands for resonance (B). Compared with Fig. 1, the relative intensity ratio $(B)/(A)$ is larger due to a shorter repetition delay. Nevertheless, this does not change the shape of either spectra.

cal properties of the system. The molecules surrounded by O_2 are no longer free to rotate. Nevertheless, O_2 intercalation appears to have an undetectable effect on the structure of the system (x-ray diagrams are identical for pure solid C_{60} and the intercalated solid[12]), and on the other hand a large effect on the rotation of the molecules. These considerations could explain some apparently inconsistent results recently observed: samples with almost identical crystallographic characteristics sometimes present very different thermodynamic behaviors, with an orientational order transition temperature shifted a few degrees from the usual value of 256 K.[13] Oxygen intercalation can be at the origin of such a behavior.

We have also to note that if molecular oxygen easily intercalates C_{60}, other atoms or molecules of similar sizes should also do the same: N_2 and Ar have already been identified,[14] but some others, such as xenon, sulfur, selenium, or tellurium, have to be investigated in detail. In particular, N_2, which is the most abundant species in the atmosphere and has a size very similar to oxygen, is expected to intercalate solid C_{60}. Work is in progress to study these phases.

ACKNOWLEDGMENT

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