

Solid State ^{13}C and ^1H NMR Investigations on $\text{C}_{60} \cdot 2$ ferrocene

J. Rozen*, R. Céolin†, J. L. Tamarit**, H. Szwarc‡ and F. Masin*

**Matière Condensée et Résonance Magnétique, Faculté des Sciences, Université libre de Bruxelles, Boulevard du Triomphe, CP 232, 1050 Brussels, Belgium*

†*Faculté de Pharmacie, Laboratoire de Chimie Physique, 4 avenue de l'Observatoire, 75270 Paris Cedex 06, France*

***Departament de Física i Enginyeria Nuclear, ETSEIB, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Catalonia, Spain*

‡*Laboratoire de Chimie Physique, UMR 8000, Université Paris Sud, CNRS, bâtiment 490, 91405 Orsay Cedex, France*

Abstract. Previous X-Ray experiments[1] have revealed the structure of the crystal thanks to the apparent immobility of the molecules. NMR studies demonstrate that the C_{60} molecules and the ferrocene molecules are in fact moving fast enough to average the magnetic interactions. This is shown by the temperature evolution of the resonance curve and by the shape of the CP-MAS spectrum at room temperature. Further investigations allow to assert that the C_{60} molecules are undergoing 3D rotations and that Cp cycles of ferrocene are subject to planar rotations. Finally, analysis of the spectra at low MAS frequency leads to the conclusion that there are two kinds of Cp cycles.

INTRODUCTION

$\text{C}_{60} \cdot 2$ ferrocene is one of the only crystals containing fullerene molecules whose structure has been fully identified by X-Ray diffraction. This is due to their apparent immobility. At room temperature, the unit cell is triclinic and space group is $P\bar{1}$. Each molecule of ferrocene has a Cp cycle parallel to a pentagonal face of the neighboring C_{60} . The inter-plane distance is 3.3 Å, which is typical when π -interactions occur between aromatic molecules. In a molecule of ferrocene, the two cycles are almost parallel, the Cp-Fe-Cp angle is 177.8°, and they are slipped sideways by 0.8 Å.

Previous NMR experiments[2] have concluded that the frequencies observed in the solvate are similar to those of the pure crystals: 143.9 ppm for the molecules of C_{60} and 69.5 ppm for those of ferrocene. This excludes any charge transfer between the two kinds of molecules and any conductive property.

In this study, the absence of these electronic correlations between the molecules is confirmed and new features about molecular motions and magnetic properties is reported.

EXPERIMENTAL

The NMR spectrometer used is a *Bruker MSL 300*. The magnet generates a field of $7.05 T$.

Two series of experiences are reported. The first is done at room temperature on 1H using CP–MAS and decoupling in the probe *HP WB 73A MAS 4*. The 90° pulse has a length of $5 \mu s$ and the contact time is $5 ms$. The second is done on ^{13}C between $54 K$ and $294 K$ in the probe *HP LP 50*, the temperature being regulated by a *Oxford ITC4*.

The MAS spectra obtained at room temperature have been treated with the Bruker *WIN – MAS* software using the method of Herzfeld and Berger[3] in order to calculate the chemical shift tensor.

RESULTS AND DISCUSSION

Fullerene Dynamics

A MAS frequency of $184 Hz$ has been used at room temperature to obtain the ^{13}C spectrum of fullerene. The central peak is observed at $143.7 ppm$, cf. FIGURE 1. This is slightly inferior to the frequency observed for the pure crystal at room temperature ($143.9 ppm$). This shift is very small and confirms that no charge transfer occurs in the solvate.

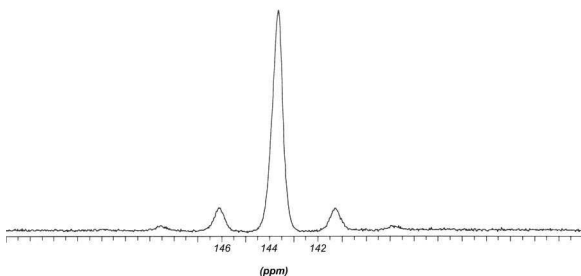


FIGURE 1. ^{13}C CP–MAS spectrum of fullerene molecules in $C_{60} \cdot 2 ferrocene$ at room temperature under a MAS frequency of $184 Hz$.

The components of the chemical shift tensor, reported in TABLE 1, are almost identical ($\delta \ll d$). This leads to the conclusion that, at room temperature, the molecules of C_{60} are undergoing fast isotropic rotations. Indeed, the correlation time has to be much smaller than the length of the signal ($FID \simeq 0.03 s$) in order to average the magnetic interactions.

This result seems to contradict X–Ray experiments which let to think there is no mobility in the crystal. NMR is sensitive to individual ^{13}C on a fullerene molecule whereas X–Rays observe all the carbon atoms without distinction. Nuclear Magnetic Resonance is therefore affected by discrete rotations leading to symmetry–equivalent orientations while X–Rays are not as only an average orientation is observed.

TABLE 1. Components of the chemical shift tensors at room temperature in the solvate. CP1 is noted for the left set of C_5H_5 peaks and CP2 for the right set. (All values in ppm)

	d_1	d_2	d_3	\bar{d}	δ	η
C_{60}	144 ± 0.8	145.9 ± 0.7	141.2 ± 0.7	143.7	2.5 ± 1.4	0.76 ± 0.59
CP1	96	96.3	23.8	72	48.2	0
CP2	97.2	97.2	17.3	70.6	53.3	0

Ferrocene Dynamics and Magnetic Organization

The ferrocene ^{13}C spectrum observed at a MAS frequency of $1196 Hz$ is presented on FIGURE 2b. It is unexpected since it contains information that had not been reported previously (cf. below); there are two sets of peaks. Once again the deviation of the central frequency is very small ($69.5 ppm$ in a ferrocene crystal). This information is in tune with the equivalent finding for fullerene molecules which excludes charge transfer. As seen in the lower part of TABLE 1, the components of the chemical shift tensors can be separated in d_{\parallel} and d_{\perp} ($\eta \simeq 0 ppm$), which means cycles are undergoing fast uniaxial isotropic rotations compared with the observation time ($FID \simeq 0.035 s$). This is confirmed by the evolution of the 1H peak width between $54 K$ and room temperature reported on the left part of FIGURE 3. The second order moment, M_2 , is reduced upon heating which is typical when molecular movements occur.

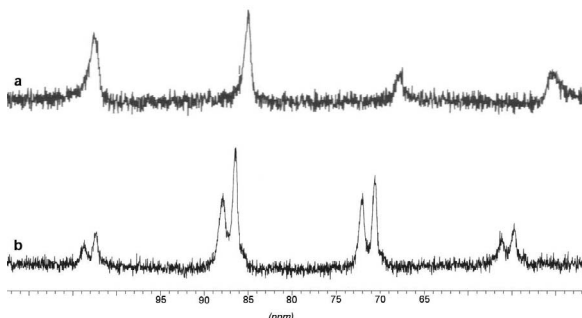


FIGURE 2. Ferrocene ^{13}C CP–MAS spectra at room temperature (a) in the pure crystal at a MAS frequency of $1206 Hz$, (b) in the $C_{60} \cdot 2 ferrocene$ solvate at a MAS frequency of $1196 Hz$.

That two sets of peaks separated by less than $1.5 ppm$ are present is particular of the $C_{60} \cdot 2 ferrocene$ solvate. It has been checked that it is not the case in a ferrocene crystal under similar conditions, cf. FIGURE 2a. In order to get a qualitative idea of the magnetic organization, the areas which are proportional to the number of concerned atoms have been compared. This reveals that 50% of the carbon atoms present in ferrocene contribute to each set. The unit cell contains two molecules of ferrocene and therefore, four crystallographically inequivalent C_5H_5 cycles. It can be concluded that there are two kinds of C_5H_5 cycles magnetically inequivalent in the solvate.

Shannon et al.[4] have shown that a crystal of ferrocene has a particular behaviour when the CP–MAS technique is used. For a given decoupling field, it seems that the width of the peak, Δ , increases when the MAS frequency is risen. From further experiments on deuterated ferrocene, it is concluded that MAS frequencies have negative consequences on the spin–spin decoupling. The right part of FIGURE 3 shows that this effect is observed in the $C_{60} \cdot 2$ ferrocene solvate where the two peaks are superposed as the MAS frequency is increased. The first NMR spectrum of the solvate was obtained at 4000 Hz under a smaller decoupling field, which could explain why the two peaks were not then distinguished.

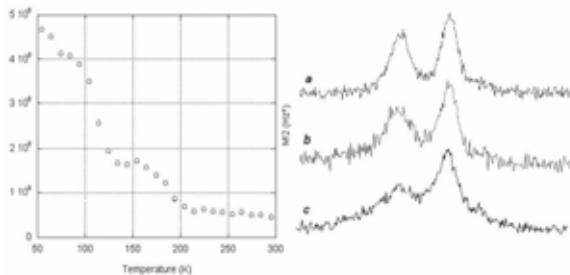


FIGURE 3. λ On the left λ Variation under temperature change of the 1H peak second order momentum. λ On the right λ ^{13}C CP–MAS spectra at room temperature of ferrocene in the solvate. (a) $v_{MAS} = 1196 Hz$, (b) $v_{MAS} = 2000 Hz$, (c) $v_{MAS} = 4001 Hz$.

CONCLUSION

Comparing the spectra with those of pure crystals, this work has confirmed the absence of conductivity properties in the solvate. Secondly, it has been shown for the first time that, in the solvate, there are two magnetically inequivalent kinds of C_p cycles in ferrocene since two sets of peaks show up in the CP–MAS spectrum. But the main contribution of the experiments is the observation of fast reorientational motions within the solvate lattice, motions that X–Rays had been unable to detect.

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REFERENCES

1. J. D. Crane, P. B. Hitchcock, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc.*, 1764 (1992).
2. E. Shabanova, K. Schaumburg and F. S. Kamounah, *Can. J. Anal. Sci. Spectrosc.*, **43** (2): 53 (1998).
3. J. Herzfeld and A. E. Berger, *J. Chem. Phys.*, **73** (12): 6021 (1980).
4. I. J. Shannon, K. D. M. Harris and S. Arumugam, *Chem. Phys. Lett.*, **6**: 588 (1992).