# The Orientation of Graphite Planes in Carbon Fibers
## via Carbon-13 NMR Spectroscopy

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The Nuclear Magnetic Resonance (NMR) chemical shift for the carbon atoms of a graphene plane (as in graphite, graphite fibers, charcoal, etc.) is a unique indicator of the orientation of the normal to that plane with respect to the magnetic field direction. Here, we use this fact to show that in a graphite fiber, 85% of the plane normals are perpendicular to the fiber axis, while the rest are nearly random. We report $^{13}C$ NMR spectra for highly oriented pyrolytic graphite (fig. 1), a charcoal (fig. 2) and a highly graphitized carbon fiber (fig. 3).

The HOPG specimen (Union Carbide) is a square ca 8 mm on a side, of thickness ca 0.8 mm in the c-direction. The charcoal is from a set of charcoals under test at NRL in air purification applications, labeled HAA7. The graphite fibers are TP 4104B, pitch based (Union Carbide)[1]; they were intercalated to a deep purple color with $AsF_5$, indicative of stage I. Spectra were recorded on a Bruker CXP spectrometer at 50 MHz (HOPG) and on a JEOL FX6Q at 15 MHz.

The site symmetry of a carbon atom in a graphene plane includes a 3 fold axis normal to the plane. Thus there are at most two principal values for the chemical shift tensor: $\delta_\parallel$, the shift observed for the magnetic field parallel to the c-axis, and $\delta_\perp$, the shift observed when the magnetic field lies anywhere in the graphite plane. For other angles,

$$\delta(\beta) = [\ \delta_\parallel + \delta_\perp + (\delta_\parallel - \delta_\perp)\cos 2\beta]/2 \qquad (1)$$

where $\beta$ is the angle between the c-axis and the magnetic field. For HOPG we are able to choose $\beta$ and record a spectrum; such are given in fig. 1. For $B_0$ in the plane, the spectrum is relatively sharp, while for $B_0$ parallel c the spectrum is 50 ppm wide. We have no explanation for this "excess" width yet. The median chemical shift as a function of the angle $\beta$ is

$$\delta(\beta) = (91 - 89 \cos 2\beta) \text{ ppm} \qquad (2)$$

so that $\delta_\perp = 180$ ppm and $\delta_\parallel = 2$ ppm.

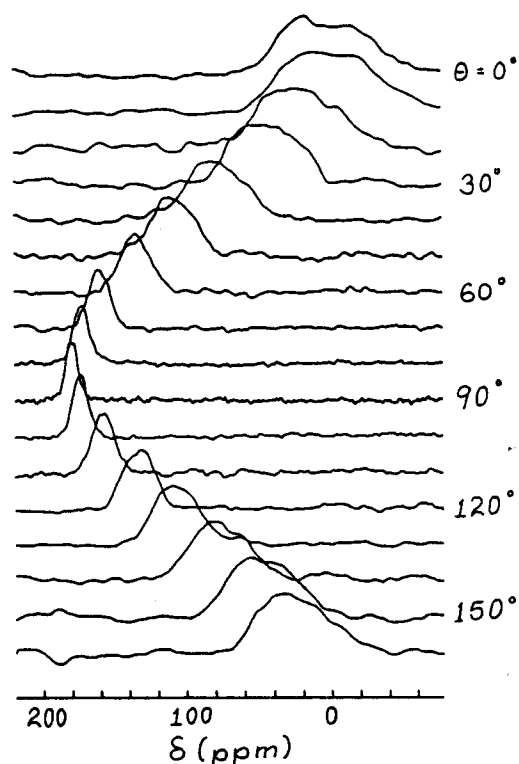As an experimental example of the spectrum for a randomly oriented collection



Fig.1. $^{13}C$ NMR spectra of HOPG at 50 MHz as a function of the angle between the c-axis and the applied magnetic field.

of graphene planes we show a spectrum of a charcoal (fig. 2). This is a severely broadened axially symmetric powder pattern. Such a pattern should be marked by a step discontinuity on the right side (at $\delta_\parallel$) and by an infinity on the left (at $\delta_\perp$). The infinity is broadened but apparent. The step appears completely washed out, perhaps due to the same broadening mechanism as for the HOPG. As will become more apparent, use of the $^{13}C$ shift tensor in fiber orientation studies really requires the spectrum in the vicinity of $\delta_\parallel$ to be sharp, and figs. 1 and 2 (as well as a $^{13}C$ spectrum for native graphite fibers)

suggest that this resolution is not available. For reference, the probability density function (spectrum) for the axial powder pattern is

$$P_A(\delta) = [(\delta_\| - \delta_\perp)(\delta - \delta_\perp)]^{-\frac{1}{2}}/2 \quad (3)$$

But we have found that ^{13}C spectra for intercalated graphite are in many cases sharper than those shown for graphite in fig. 1. In particular, the intercalation of AsF$_5$ gives quite sharp ^{13}C spectra[2]. Even the AsF$_5$ [19]F spectra thereof are orientation dependent, and can be used for finding orientation distributions of graphene planes in fibers[3]. The AsF$_5$ also serves to reduce the relaxation time $T_1$ for the carbon at all orientations, making signal averaging for increased S/N profitable. The chemical shift depends on intercalant and stage as well as on the angle.

In fig. 3 is a spectrum for a collection of fibers in a 10 mm pyrex tube, rather carefully packed to achieve mutual parallelism of the fibers among themselves as well as with the tube cylinder axis; these fibers are intercalated with AsF$_5$; the magnetic field is perpendicular to the cylinder axes of the pyrex tube. The spectrum is u-shaped with "infinities" at both $\delta_\perp$ and $\delta_\|$. The high intensity at $\delta_\|$ tells us that a larger fraction of graphene c-axes are parallel to the magnetic field than for a random assembly of planes (cf fig. 2).

The first model we take for the graphite fiber is the desired one in which all graphine planes contain the fiber axis, i.e. all graphite c-axes are perpendicular to the cylinder axis. For $B_0 \perp c$ this would give the two-dimensional powder anistropy pattern, the equation of which is

$$P_{2D}(\delta) = 2[(\delta_\| - \delta_\perp)^2 - (2\delta - \delta_\| - \delta_\perp)^2]^{-\frac{1}{2}}/\pi \quad (4)$$

This function is u-shaped and symmetric about $\delta_{av} = (\delta_\| + \delta_\perp)/2$, and has infinities at $\delta_\perp$ and $\delta_\|$. The experimental spectrum of fig. 3 is not symmetric and has more intensity on the left (at $\delta_\perp$) than the model predicts.

We interpret the data on the basis of a second model which consists of a fraction $F_A$ of axial spectrum, eq. (3), (random orientation of c-axes) and a fraction $F_{2D}$ (= 1-$F_A$) of 2D-anisotropy pattern, eq. (4). We extract these fractions by using the facts that $P_{2D}$ is symmetric and $P_A$ is not. We use the steep sides of fig. 3 to find the center of the spectrum $\delta_{av}$, and to divide the spectrum into a left and a right side. By integration (weighing) the two sides we find the difference D and sum S of the two sides of the observed spectrum. Eq. (3) and (4) allow us to do the same for the theoretical model. The random fraction is then
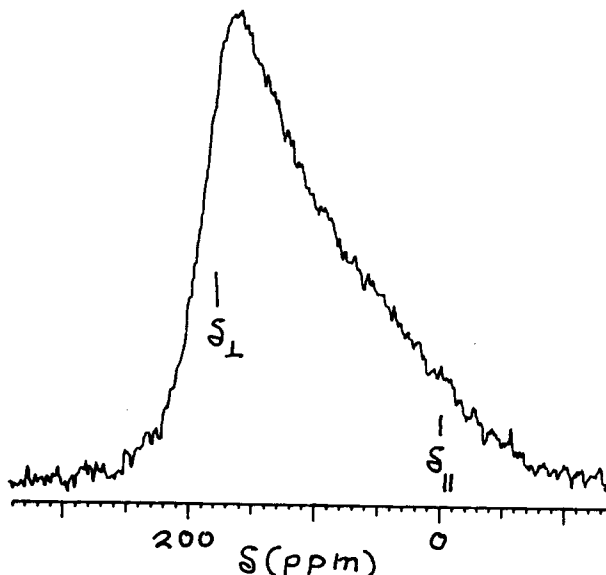
$$F_A = (D-S)/(\sqrt{2} - 1) \quad (5)$$
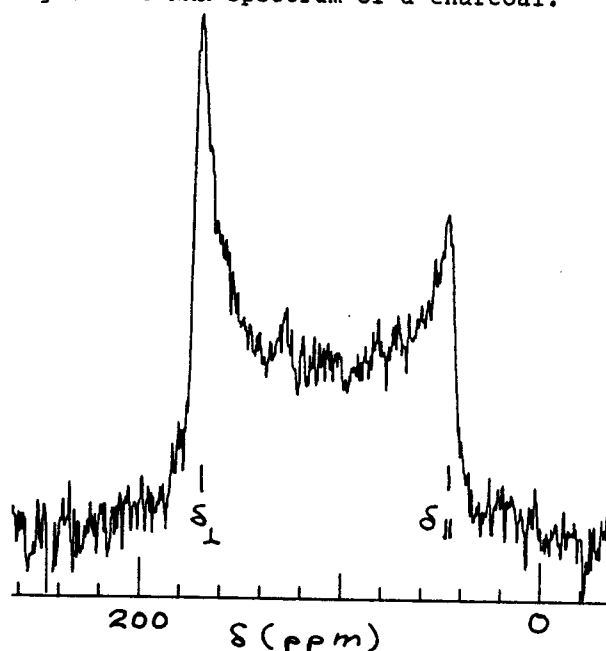


Fig.2 ^{13}C NMR spectrum of a charcoal.



Fig.3 ^{13}C NMR spectrum of TP4104B graphitized carbon fibers which have been intercalated with AsF$_5$. The applied field is normal to the fiber axes.

which for D ~6% yields $F_A$ = 15%. We conclude that 85% of the graphene planes of this fiber are oriented so as to produce fibers of maximum modulus.

## References

1. Properties of TP4104B fiber summarized in D. D. Dominguez, J .L. Lakshmanan, E. F. Barbano, and J. S. Murday, in "Intercalated Graphite" MRS Symp. Proc. 20, 63 (1983).
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3. H. A. Resing, Gerald Ray Miller, M. J. Moran, J. P. Reardon, D. D. Dominguez, F. L. Vogel, and T. C. Wu, Extended Abstr., 15th Carbon Conference, 1981, p369.