RAMAN SPECTRA AND CHARACTERIZATION OF CARBON MATERIALS

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The Raman spectra of carbon materials have been thought to comprise just two lines, at 1580 and 1360 cm^{-1} (1-6); but recent studies (7,8) have revealed several additional lines for both crystalline graphite and disordered carbons. Some results of an ongoing investigation for the behavior of these lines and of the characterization of various carbon material types are described here.

Spectra were excited with 488 (sometimes 514.5) nm radiation from a CRL 52 Ar^+/Kr^+ laser and scanned with a Spex 1401 double monochromator/photomultiplier detector with a spectral slit width setting of 8 cm^{-1}. Many materials were studied including natural graphite single crystals (NGSC); compression-annealed pyrolytic carbon (CAPC); "massive" (MPC) and fluidized-bed (FBPC) pyrocarbons; glassy carbons (GC); and carbon fibers from PAN, rayon, and pitch. Virgin or fracture surfaces were used; but also the effects of mechanical polishing, ion-bombardment etching, reactor irradiation, and oxidation were observed for some materials. The FBPCs and GCs were heat treated over the range 1000-3000°C. Spectra were analyzed in terms of line position, integrated intensity I, and full width at half height W using an analogue type curve synthesizer and Gaussian line shapes.

The positions and some characteristics of the lines observed are summarized in Table I. Polarization studies still in progress suggest that G_1', G_2', G", and perhaps D and D' are polarized but that G is not. The studies also suggest that all lines (except perhaps G") result from in-plane vibrational modes. The previously reported G and D lines have been ascribed to E_{2g} and A_{1g} vib. modes respectively (1). D' is responsible for the blue-shift of the apparent G line to $\cong 1600$ cm^{-1} in very disordered carbons. In such carbons both G and D appear as broad peaks on very broad pedestals. The G' band appears to be the first overtone of D. D is silent in crystalline graphite, while G' is absent or attenuated in very disordered carbons and damaged graphites where D is strong, though the two co-exist in annealed carbons. This suggests that the mode(s) involved exhibit electro-optic anharmonicities (9). It also seems significant that only one line (1370 cm^{-1}) is observed in hexagonal BN.

The structure-sensitivity of the spectral features makes Raman spectroscopy a useful technique for carbon materials characterization. Representative spectra are shown in Fig. 1. The CAPC cleavage spectrum is typical of crystalline graphites, comprising a sharp G, weak G", and strong G_1',G_2'. Damage by ion etching attenuates G' and generates D & D'; similar effects result from polishing layer edges. For GC (1000°C); D, D', and G overlap and G' is absent; but it develops as a symmetrical band with increasing HTT. MPCs exhibit G', D', G, and D but I and W depend on deposition temperature (1600-2500°C).

The development with HTT of the widths W_G,W_D and the relative integrated intensities I_D/I_G, $I_{G'}/I_G$ for several carbons are compared in Fig. 2. The GCs were obtained from Beckwith and Sigri; the FBPCs were deposited from propylene. The graphitizability of C-13 (1150°C) was fairly high while that of C-4 (1350°C) was medium according to diamagnetic, density, and X-ray diffraction data (10). The HTT for G' appear-

ance depends on carbon type and corresponds to $W_D \leq 90$ cm^{-1}. Initial widths increase with graphitizability; final widths for the FBPCs are lower than that for GC. The major spectral evolution occurs for HTT< 2400°C, while the carbons are still disordered, and the influence of layer stacking order appears to be negligible.

The spectral characteristics of fiber carbons are sensitive to precursor/processing differences, correlate well with mechanical properties, and depend systematically on surface "orientation". In Fig. 3, I_D/I_G for lateral surfaces is plotted against that for fractured cross sections for a large number of fiber types. Disorder decreases with increasing thermo-mechanical processing, but in all cases $I_D > 0$ as expected. A pronounced trend, increasing with modulus E, for the surface to be more ordered than the interior (cross section) is evident (2). This supports other evidence for a developing sheath/core duplex structure. The strong influences of precursor and processing are clear in an I_D/I_G plot, Fig. 4. The sharp peak in PAN fibers correlates with fracture parameter behavior (11) and may be related to the influences of residual stresses and nitrogen. The high disorder in anisotropic (mesophase) pitch fibers is attributable to low processing temperatures (<2000°C). The effects of HTT ($E \leq 100$ GN/m^2) and hot-stretching (E >100) are qualitatively similar for fibers from rayon and isotropic pitch.

The Raman activity of carbons originates from in-plane lattice vibrational modes, and is responsive primarily to defects and distortion affecting the symmetry and perfection of the layer structure. As the detailed origins of the lines become better understood, Raman spectroscopy promises to evolve from a useful empirical characterization method to a sensitive probe into the nature of the structural disorder.

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TABLE I

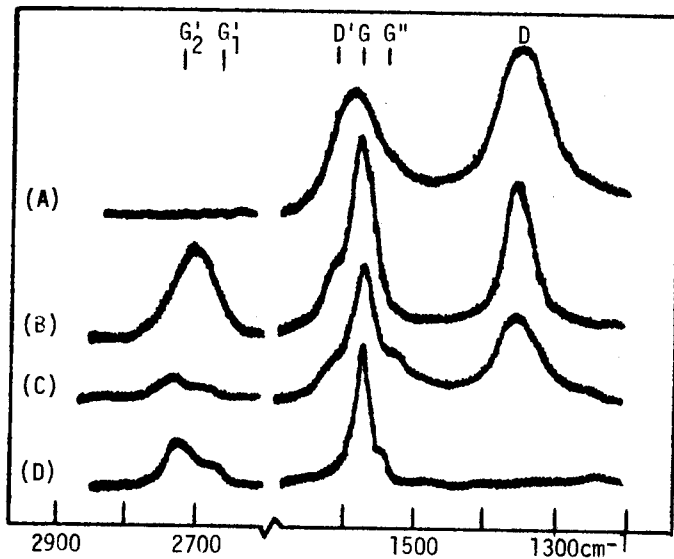| PEAK	POSITION (cm^{-1})	WIDTH (cm^{-1})	OCCURENCE	I/I_G
G	1580	$\gtrsim 20$	All carbons & graphites	1.0
G"	1560	$\lesssim 20$	Crystalline graphite	$\lesssim 0.1$
G'_1	2695	$\cong 40$	Crystalline graphite	$\lesssim 0.5$
G'_2	2735	$\lesssim 40$		$\cong 0.5$
G'	2700-2720	$\cong 75$	Annealed carbons	$\lesssim 1.0$
D	1360	$\gtrsim 40$	Disordered carbons	$\lesssim 3.0$
D'	1620	$\lesssim 45$	Disordered carbons	$\lesssim 0.4$

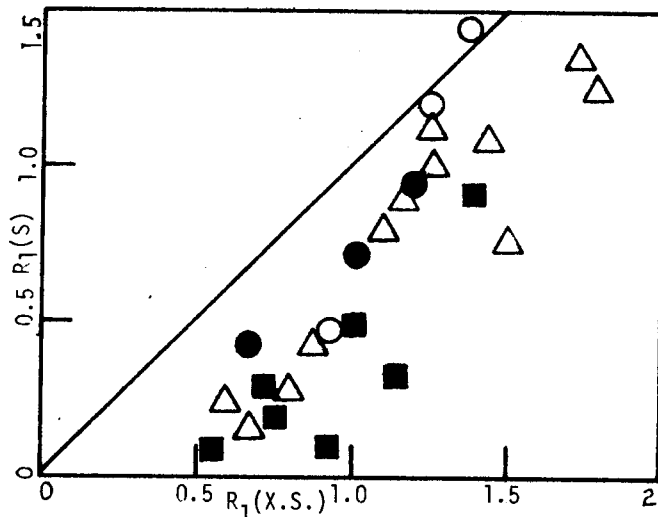Fig. 1; Raman Spectra of: (A) GC-1000°C; (B) MPC-1800°C; (C) CAPC-ion etched; (D) CAPC-cleaved.

Fig. 3; $R_1=I_D/I_G$(SURFACE) vs $R_1=I_D/I_G$(CROSS SECTION) for carbon fibers.

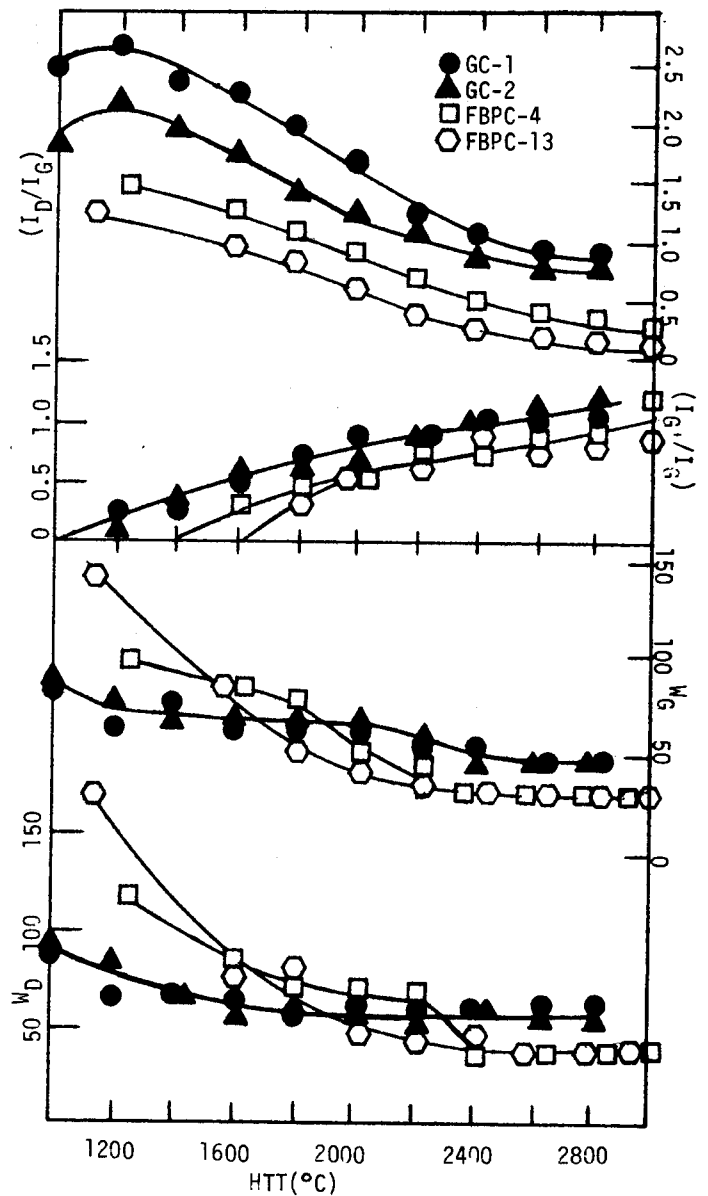Fig. 4; $R_1=I_D/I_G$(SURFACE) vs modulus for carbon fibers. $\longrightarrow$

Fig. 2; I_D/I_G & $I_{G'}/I_G$ vs HTT and W_G & W_D vs HTT for GC and FBPC.