

LASER RAMAN STUDIES ON CARBONS

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Abstract—Laser Raman spectra were studied of natural graphite (SP-1) and carbonaceous materials including pyrolytic graphite, carbon black, glassy carbon, coal, "white" carbon and sputtered carbon. All of these carbons have two Raman bands at 1580 cm^{-1} and 1360 cm^{-1} , except for natural graphite which has a single sharp Raman band at 1580 cm^{-1} . The relative intensity of the 1360 cm^{-1} band to the 1580 cm^{-1} band and the half band width increase going from graphite through glassy carbon to carbon black. The 1360 cm^{-1} band in glassy carbon becomes sharper and stronger with the increase of heat-treatment temperature (HTT), while the addition of iron to the glassy carbon matrices results in a decrease in intensity and half band width of this band with increasing HTT and iron content. Sputtered carbon and "white" carbon, prepared from graphite irradiated by a high power laser, showed an additional broad band around 2140 cm^{-1} . This band is believed to originate from conjugated acetylenic bands ($-\text{C}\equiv\text{C}-$)_n.

1. INTRODUCTION

The microstructure of carbonaceous materials has been studied in detail by X-ray and electron diffraction, and optical microscopy. A great interest has been taken in the structural aspects of glassy carbon and several structural models have been proposed for this carbon material having curious properties. Some of these models suggest that glassy carbon is constructed of all possible types of carbon-carbon bonds: single (C—C), double (C=C), triple (C≡C) and their conjugated forms. These carbon bonds are expected to have different vibrational frequencies, depending on their bond length and bond order. An attempt was first made to obtain Raman spectra of graphite and carbon materials including activated charcoal, carbon black and glassy carbon by Tuinstra and Koenig [1] and later Friedel and Carlson [2, 3]. A single

Raman band has been observed at 1575 cm^{-1} in single crystals of graphite and assigned to a doubly degenerate deformation vibration of the hexagonal ring corresponding to the E_{2g} mode of graphite with D_{6h}^1 crystal symmetry. In polycrystalline graphite an additional band was observed at 1355 cm^{-1} and attributed to a crystalline size effect [1, 4]. Tuinstra and Koenig suggested that the intensity ratio of the 1355 cm^{-1} to the 1575 cm^{-1} Raman band is directly related to the "amount of crystal boundary" which can be expressed by the reciprocal of the average crystal diameter, L_n , in the graphite plane, as determined by X-ray diffraction methods. Laser Raman spectroscopy may therefore be regarded as a promising tool to gain additional insight into the complex microstructural nature of carbonaceous compounds.

This report is concerned with the general behavior of Raman spectra obtained from natural graphite and other carbonaceous materials and the relationship of these spectra to the chemical structure of carbons.

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2. EXPERIMENTAL

Laser Raman spectra were obtained from carbonaceous materials, including natural graphite (SP-1) from the Carbon Products Division of Union Carbide Corporation, a very fine carbon black Carbolac-1 (Cabot Corporation), glassy carbons[5], pyrolytic graphite (General Electric Company), anthracite (90.9 per cent, Pennsylvania Buck Mountain), sputtered carbon and "white" carbon[6] produced by high power laser illumination. Studies were also carried out employing polynuclear aromatic and acetylenic hydrocarbons of known composition and structure as model compounds for comparative purposes.*

Raman spectra were obtained on a SPEX Ramalog (1401) equipped with an RCA 250 mW Ar ion laser. Most of the measurements were carried out employing the 4880 Å line. On occasion, the 5145 Å line was used to eliminate spurious bands caused by fluorescence effects. A Spectra Physics 20 mW He-Ne laser (6328 Å) was also used as an excitation source for the polynuclear aromatic model compounds. The spectra were measured on powder spread over a glass plate or pressed powder pellets. For glassy carbons from furfuryl alcohol[5], plate shaped specimens were prepared for the Raman studies. The incident laser beam was focused onto the flat surface of the specimen mounted on an ordinary single crystal goniometer. The angle between the laser beam and the sample surface was variable in the range 0°C to 25°C so as to minimize Rayleigh scattering effects. The scattered Raman light from the sample surface was collected and focused on the entrance slit of the spectrometer through a camera lens. The Raman spectra were recorded with a spectral slit width of up to 10 cm⁻¹ and a sensitivity of 10⁻⁹ Å. For the purpose of recording Raman spectra of "white" carbon,

glassy carbons in plate form and pressed graphite pellets were irradiated for 2 min by a 40 W CO₂ laser (about 60 kW cm⁻² power density) and by a 40 MW Ruby laser (about 10 GW cm⁻² power density) with pulse duration in the nanosecond range in an upward flowing helium stream.

The high power Ruby laser illumination caused white or gray craters with a diameter of about 0.5 mm. These craters were surrounded by a material of a gray colour. In glassy carbon plates heat treated at temperatures ranging from 970°C to 2000°C, illumination by the CO₂ laser resulted in well defined "white" rings or sometimes horseshoe shaped "white" deposits surrounding the crater. These white ring deposits were not observed on graphite pellets and pyrolytic graphite rods by the CO₂ laser illumination, only craters being produced. Sputtered carbons were obtained on KBr crystals and glass plates using an MRC, Model 8632 R₁/DC sputtering module. The sputtered carbon thicknesses ranged from 500 Å to 2.4 μm.

Band intensities for the 1355 cm⁻¹ and the 1580 cm⁻¹ Raman bands were calculated from the product of band height and half band width.

3. RESULTS AND DISCUSSION

Representative tracings of Raman spectra are shown in Fig. 1. Crudely pulverized natural graphite (SP-1) gives a weak but distinct Raman band at 1355 cm⁻¹ in addition to the strong 1580 cm⁻¹ band. The same natural graphite ground to a particle size of less than 1 μm exhibits only one Raman band at 1580 cm⁻¹. Tuinstra and Koenig[1], in their related study, suggested a linear relationship between the intensity ratio of the 1355 cm⁻¹ to the 1580 cm⁻¹ Raman bands and the reciprocal of crystallite diameter, L_n , as measured by X-ray diffraction line broadening. The L_n values of the crudely pulverized graphite and the finely ground material were determined by X-ray diffraction techniques and found to be nearly the same, 1600 Å and 1500 Å, re-

*Samples of 1,1'-Dianthranil poly-yne were kindly supplied through the courtesy of Prof. M. Nakagawa and Prof. S. Akiyama, Osaka University, Osaka, Japan.

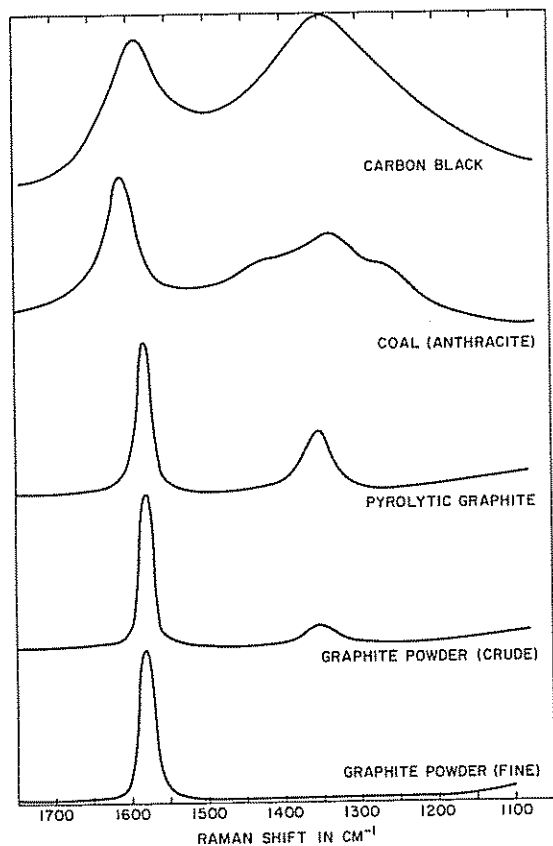


Fig. 1. Raman spectra of graphites, coal and carbon black.

spectively. Thus, this finding does not confirm the general conclusion by Tuinstra and Koenig with regard to crystalline size and the intensity ratio of the Raman bands. The Raman spectrum of pyrolytic graphite is very similar to that of the crude particles of natural graphite except that the former has a slightly stronger 1355 cm^{-1} band than the latter. The pyrolytic graphite used in this study has an L_n of approximately 320 \AA . The intensity ratio of the two Raman bands undoubtedly increases with decreasing crystallite diameter in this case. Carbon black and anthracite give strong 1355 cm^{-1} bands with considerable line broadening and, in some cases, the distinct appearance of additional bands close to the 1355 cm^{-1} band. The Raman

spectra of anthracite heat-treated at 1000°C and 1500°C were also measured in our laboratory along with the untreated samples. The calcined samples of anthracite gave Raman spectra exhibiting much sharper bands than the original coal and showed spectral changes identical to those of glassy carbons with the same thermal history.

Figure 2 shows Raman spectra of glassy carbons prepared from polyfurfuryl alcohol (PFA) heat-treated at temperatures ranging from 500°C to 2000°C . The Raman spectra show a distinct increase in intensity and narrowing of band width of the 1355 cm^{-1} band with increasing HTT. As in the case of natural graphite powders, no quantitative correlation was observable between Raman

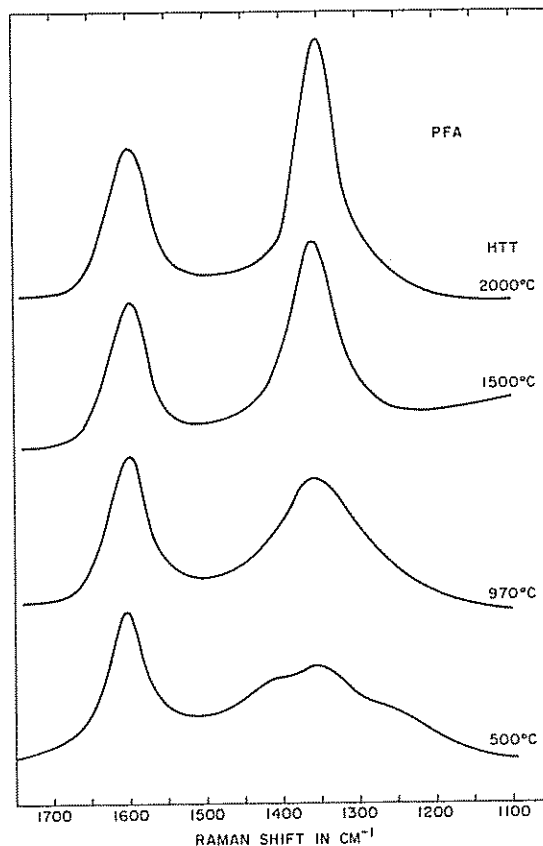


Fig. 2. Raman spectra of glassy carbons prepared from polyfurfuryl alcohol (PFA).

intensity and crystallite size. The glassy carbons used in this study had extremely weak and broad X-ray diffraction peaks from the (110) plane so as to render the determination of L_n values unfeasible. The band width of the 1355 cm^{-1} band decreases with increasing HTT and approaches that of the 1580 cm^{-1} band at higher HTT.

Addition of iron to the glassy carbons resulted in a decrease of the intensity of the 1355 cm^{-1} band and the spectral band width, as shown in Fig. 3. A marked decrease in the width of this band was found in iron containing glassy carbons prepared at temperatures from 600°C to 700°C , as can be seen in Fig. 4. This suggests a temperature range in which sudden structural changes take place in the carbonaceous matrix. X-ray diffraction measurements on iron-doped glassy carbons indicated extensive narrowing of the diffraction peak from the (002) plane in this temperature range. However, the 1580 cm^{-1} band is insensitive to these changes and shows only a gradual decrease in Raman band width with increasing HTT. Therefore, the band width of the 1355 cm^{-1} band may be related to the growth of polycondensed aromatic planes.

Figure 5 shows changes in the intensity

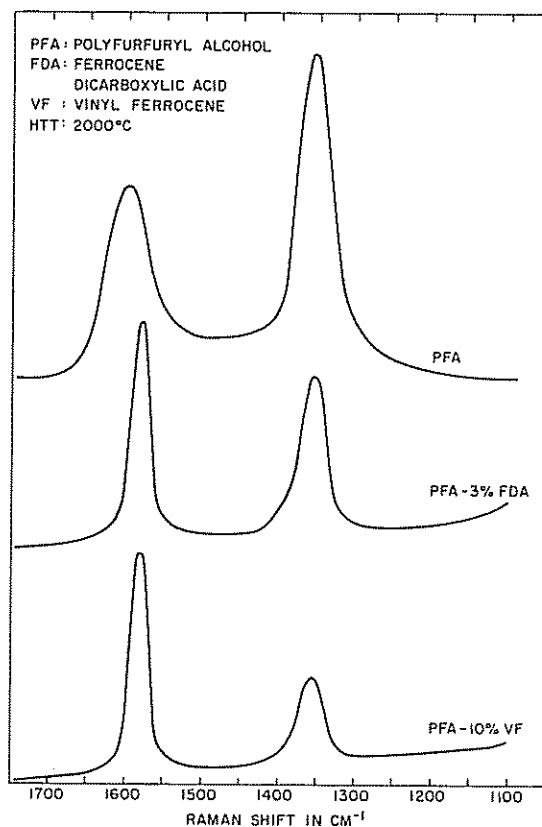


Fig. 3. Raman spectra of PFA and iron-containing glassy carbons.

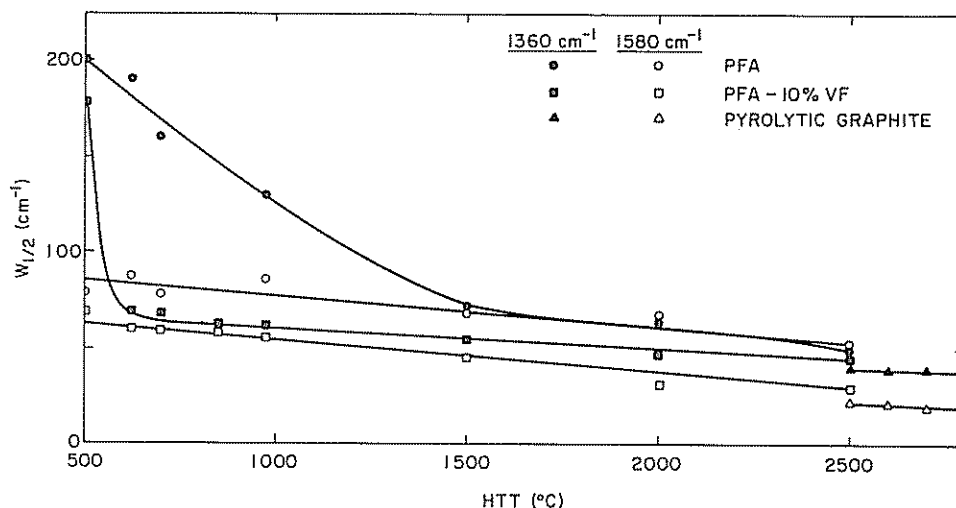


Fig. 4. Change in half band width of the Raman bands with HTT.

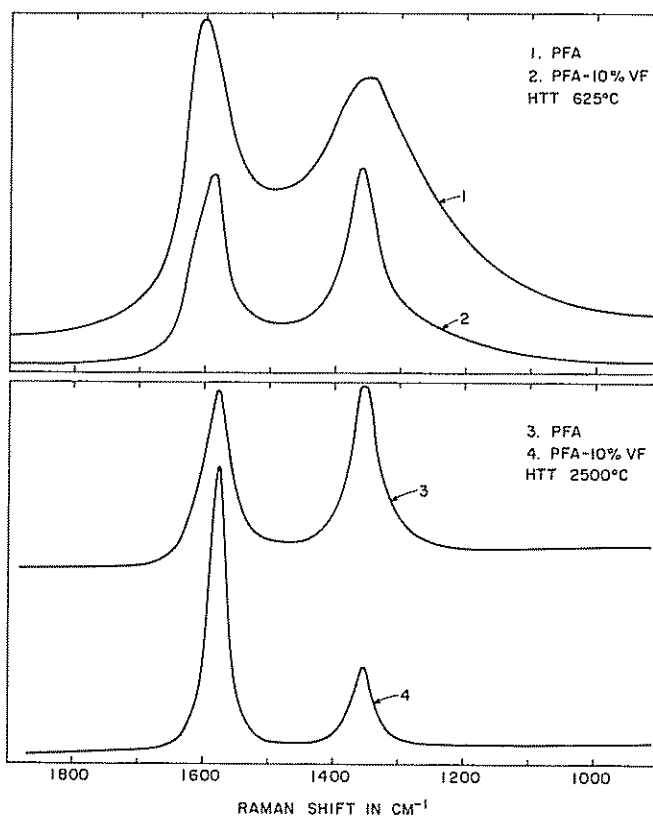


Fig. 6. Raman spectra of PFA and PFA-10 per cent VF carbons heat-treated at 625°C and 2500°C.

hybridization. If glassy carbons contain diamond type and poly-yne type carbons, one would expect strong Raman bands from polyynes at 2000 cm^{-1} to 2200 cm^{-1} and for sp^3 type carbons from 800 cm^{-1} to 1200 cm^{-1} . Diamond itself has a sharp and strong Raman band at 1332 cm^{-1} . Therefore, no evidence was obtained for the existence of chemical bonds other than trigonal carbon bonds, at least from Raman spectra. Ergun *et al.*, have made a detailed analysis of the structure of a glassy carbon using the Fourier transform technique and suggested that glassy carbon is made up of distorted hexagonal rings[10]. These include 1,3- and 1,4-quinoid structures of graphitic layers in which one third of the bonds are shorter than the rest. The two-dimensional unit cells of these quinoid structures are a rectangular and contain 4 atoms,

the three dimensional unit cells being orthorhombic. The number of Raman and infrared bands expected in the quinoid structures can easily be enumerated using the group theoretical method. For these quinoid structures, six Raman and three infrared bands are predicted. Therefore, these structures do not satisfy the experimentally observed Raman spectra of glassy carbons. Generally a lowering of lattice symmetry and an increase in the number of atoms in a unit cell lead to an increase in the number of vibrations which can be observed in the Raman scattering and infrared absorption. A group theoretical analysis for graphite with crystal symmetry D_{6h}^+ predicts only one Raman active band. This agrees well with the experimental observations on single crystals of graphite[1] and natural graphite, as shown in Fig. 1.

Condensed aromatic hydrocarbons exhibit intense Raman bands at spectral ranges of 1340 cm^{-1} to 1420 cm^{-1} and 1550 cm^{-1} to 1650 cm^{-1} , as shown in Fig. 8. The spectral positions of these bands depend strongly on the size of the molecule and its geometrical shape. It has been found from infrared and Raman studies on organic molecules that the spectral bands due to stretching vibrations of the carbon double bond and its conjugated forms are observed around 1600 cm^{-1} . In addition to these bands, condensed aromatic hydrocarbons always give intense Raman bands around 1380 cm^{-1} , which corresponds to the vibration characteristic of the benzene skeleton. Therefore, the 1360 cm^{-1} band in

carbonaceous materials is closely associated with chemical structures consisting of condensed benzene rings.

Friedel and Carlson studied infrared spectra of graphite, coal and carbons like carbon black, activated carbon from coconut and channel black, showed that these materials have also two broad infrared bands. The frequencies of the two major infrared bands are very similar to the two Raman frequencies observed for the same material[3]. This indicates that the local symmetry of the scattering unit is low and that a local center of symmetry is absent. These can be expected for amorphous materials. The appearance of the 1360 cm^{-1} band suggests the breakdown of the usual selection rules which determine Raman and infrared activities of the vibrational modes of crystalline materials. The lowering of the symmetry of the scattering unit and the loss of translational symmetry cause all the vibrational modes to contribute to the Raman scattering and lead to the appearance of new bands and the broadening of the observed bands.

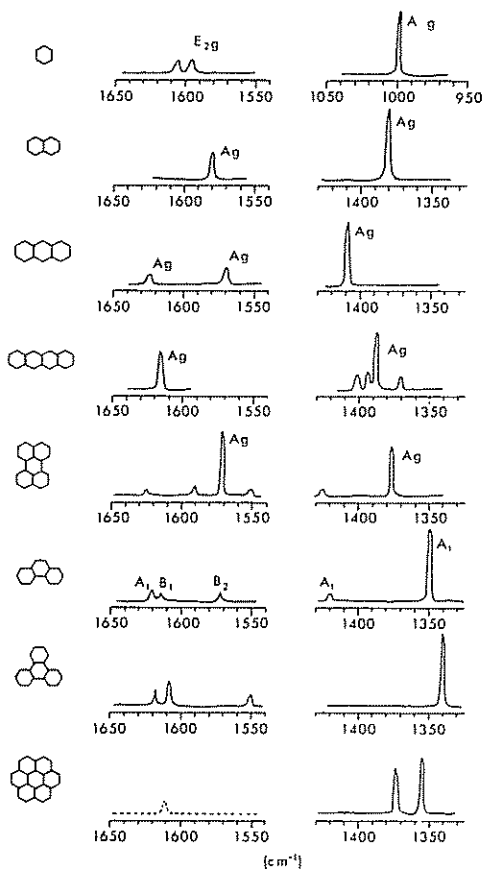


Fig. 8. Raman spectra of condensed aromatic hydrocarbons.

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