

## CHARACTERISATION OF CARBON NANOTUBE MATERIALS BY RAMAN SPECTROSCOPY AND MICROSCOPY– A CASE STUDY OF MULTIWALLED AND SINGLEWALLED SAMPLES

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Laser excited Raman scattering was measured from various carbon nanotube samples, as well as high purity graphite using an Ar<sup>+</sup> laser at different wavelengths and the variation of the band parameters was studied as a function of the excitation laser wavelength. Features in the Raman scattering have been identified and assigned to known structural and dynamical sources. Scanning electron microscopic and tunnelling microscopic pictures of two different nanotube samples contributed to the characterization of the samples as multiwalled and singlewalled carbon nanotube bundles and helped identify Raman spectral features.

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### 1. Introduction

Following the discovery of carbon nanotubes (CNT) in 1991-93 [1,2] a feverish activity has ensued to establish the chemical and physical properties of these novel carbon forms. Raman spectroscopy has proved to be useful in this field. However, the understanding of CNT Raman spectra is based on vibrational and electronic properties of pure sp<sup>2</sup> and sp<sup>3</sup> hybridized carbon allotropes, of graphite and diamond. Whereas the assignment of the strongest Raman features to specific vibrational forms has already been much investigation. In addition to Raman spectroscopy, there are a few microscopy methods, which are able to detect and qualify CNT selectively. Besides Transmission Electron Microscopy, Scanning Probe Microscopy, Scanning Tunnelling Microscopy (STM) and Atomic Force Microscopy (AFM) are widely used to determine the morphology of single CNT particles [4,5] In this paper we have used Raman spectroscopy and microscopy to characterize carbon nanotube samples.

### 2. Materials

Carbon nanotubes samples have been prepared by different methods. The multi-walled samples were prepared by Co,Fe/Al<sub>2</sub>O<sub>3</sub> catalyzed decomposition of acetylene at 1000 K. This yielded thick bundles of multiwalled tubes, which then were purified to remove Al<sub>2</sub>O<sub>3</sub> and the metal particles but contained significant amounts of amorphous carbon. The single walled nanotube sample (raw SWNT) was obtained from Nanolegde S. A., Cap Alpha, Montpellier, France. This sample produced by arc discharge technique is quoted to have purity 55% by weight, nanoparticulates between 6 and 10% weight, catalyst particles between 9 and 12 weight and

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amorphous carbon by 20-25% weight. Additionally high purity graphite BDH Laboratory (UK) was used with: particle size < 50 micrometer, purity 99.5 %, and ethanol soluble matter 0.2%.

### 3. Experimental details

Raman spectra were recorded at the Centre for Applied Laser Spectroscopy at Shrivenham, University of Cranfield (RMCS) using a high-resolution (maximum  $\sim 10 \text{ cm}^{-1}$ )  $f/7.8$  double monochromator (SPEX 1404). The spectral purity is quoted to be  $<10^{-14}$  at wavelength  $> 0.5 \text{ nm}$  from a set wavelength. The spectrally dispersed signal was recorded by a low noise photomultiplier (electron Tube-9214B) having a rise time of 2 ns and a usable spectral window of 300-600 nm. The PM dark current is quoted to be 1 nA ( $200 \text{ counts s}^{-1}$ ). The output signals from the PM were processed by a gated charge integrator electronic system (EG&G PARC Model 4420) controlled by an external computer. An  $\text{Ar}^+$  ion laser (Spectra Physics, Model 165-11) operating at several discrete wavelengths between 457.9 – 514.5 nm band was used for Raman scattering excitation. Scanning electron microscopic pictures of the MWNT sample and the scanning tunnelling microscopic pictures of the SWNT samples were taken at the Research Centre for Chemistry.

### 4. Results and discussion

In this work the constitution of CNT samples allowed us to study bundled samples. The bands in these spectra recorded for different excitation wavelengths and for both the SWNT and MWNT samples, as shown in Figs. 1 and 2 were analyzed for Lorentzian components. The present spectral analysis was based on the method published by the Dresselhaus group at the Massachusetts Institute of Technology [6-10].

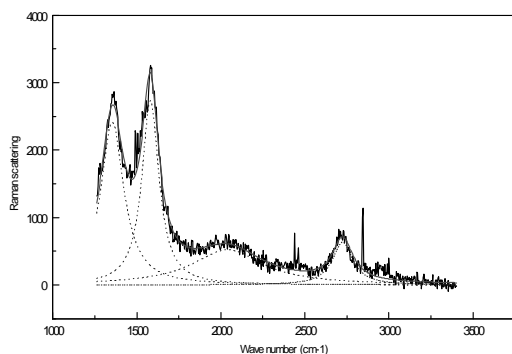


Fig. 1. Raman spectrum of MWNT bundles with laser wavelength 488 nm and Lorentzian analysis.

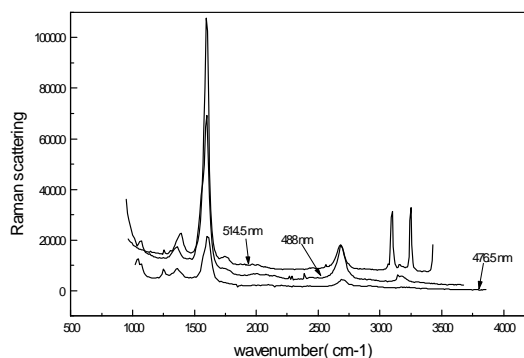


Fig. 2. Raman spectra of SWNT bundles obtained with  $\text{Ar}^+$  laser wavelengths 476.5, 488 and 514.5 nm.

The main features in the Raman spectra are first-order ones. The so-called disorder-induced D band appear at  $1354.7 \text{ cm}^{-1}$  in MWNT spectra (Fig. 1) and between  $1330$  and  $1390 \text{ cm}^{-1}$  in SWNT spectra (Fig. 2). The tangential mode G appears at  $1581.2 \text{ cm}^{-1}$  in the MWNT sample, and between  $1595 \text{ cm}^{-1}$  and  $1605 \text{ cm}^{-1}$  in the SWNT sample. The second-order G' band appears at  $2724 \text{ cm}^{-1}$  in the MWNT, and at  $2679$  and  $2689 \text{ cm}^{-1}$  in the SWNT sample.

#### 3.1. Raman spectra of the singlewalled nanotube sample

Raman spectra of CNT's contain first-order and higher-order features attributed to vibrational excitation of fundamentals and composite excitations (overtones and combination tones respectively). These features depend on the structure of the individual nanotubes which is specified by a pair of indices (m,n). These indices define the atomic coordinates for the 1D unit cell of the nanotube in question [7]. Different nanotube constructions correspond to semiconducting and metallic properties. Metallic nanotubes are defined by the condition  $2n+m=3q$ , where q is an integer.

Also one has to consider that various CNT preparative processes yield bundles of individual nanotubes. In the best case one can take Raman spectra of individual CNT's and there are a number of papers that analyse such [8].

The effect of excitation wavelength on the Raman shift for SWNT in our case is rather insignificant. This is mainly because of the small range of excitation wavelength, e.g. the largest excitation energy difference corresponds to a wavelength difference of (514.5 nm – 476.5 nm), only (0.2 eV). For the D band in the SWNT samples we find  $1363.1\text{ cm}^{-1}$  for 2.6 eV,  $1360.4\text{ cm}^{-1}$  for 2.54 eV, and  $1392.3\text{ cm}^{-1}$  and  $1389.1\text{ cm}^{-1}$  for laser energy 2.41 eV therefore there appears to be a slight wavenumber increase with decreasing laser energy. The laser energy dependence of the G band is  $1602.8\text{ cm}^{-1}$  for 2.6 eV,  $1598.9\text{ cm}^{-1}$  for 2.54 eV and  $1595.1\text{ cm}^{-1}$  and  $1601.5\text{ cm}^{-1}$  for 2.41 eV, so the G band has practically no shift. Finally the G' band in the SWNT sample is  $2698.1\text{ cm}^{-1}$  for 2.60 eV,  $2688.7\text{ cm}^{-1}$  for 2.54 eV, and  $2680.3\text{ cm}^{-1}$  and  $2694.3\text{ cm}^{-1}$  for 2.41 eV laser energy. The band has a small redshift with increasing excitation energy.

The excitation wavelength dependence of the various Raman features is mainly a resonance phenomenon. Such intense features in the spectra from those nanotubes which have their van Hove singularities (sharp features in the one-dimensional electronic state density [9,10]) in the valence and conduction bands at the appropriate position to be in resonance with the excitation laser (see Fig. 3). This allows one to characterize single CNT's and even nanotube bundles in terms of their diameter (or average diameter in case of bundles) using the diagram shown in Fig. 3 obtained from the so-called tight binding model [11] that are depicted as a function of the nanotube diameter. From the known values of laser excitation energy one can use this diagram to predict resonance with the laser energy, and also obtain some information about the nature (metallic or semiconductive) of the CNT's.

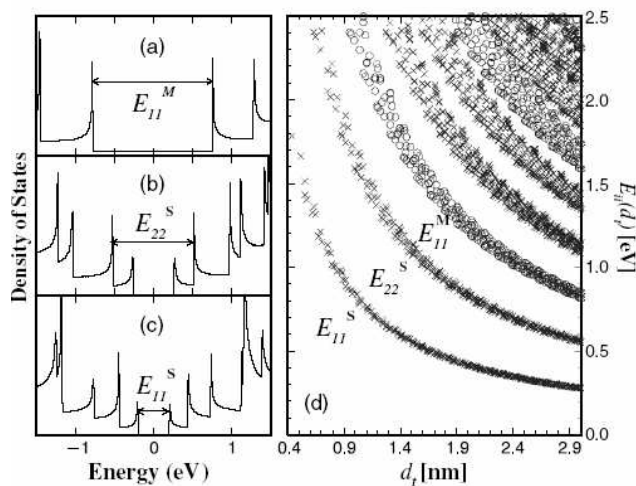


Fig. 3. Density of states of an (a) armchair SWN tube (10,10), (b) chiral SWN tube (11,9), (c) zigzag SWN tube (22,0) and the dependence of electronic transition energies on the tube diameters.

Although such a diagram is most useful when dealing with isolated CNT's, nevertheless it also gives qualitative information for CNT bundles, such as those under investigation. From Fig. 3 we see that for the range of excitation energies between 2.41 eV and 2.60 eV many metallic and semiconducting CNT's having diameters in the range 1.4 and 2.9 nm are in resonance, so the spectra shown in Figs. 1 and 2. are attributable to a grand average among CNT's in this diameter range.

There is a possibility to estimate the Raman shift of the D band from a correlation with the laser excitation energy [10] Therefore for the energy range 2.41 eV – 2.60 eV, the D band position is predicted to be between  $1338.4\text{ cm}^{-1}$  and  $1348\text{ cm}^{-1}$ . This is somewhat lower than what we found ( $1360\text{ cm}^{-1}$  -  $1390\text{ cm}^{-1}$ ) from the SWNT bundles. This is probably due to the presence of amorphous carbon in this sample, so the D band is not attributed to SWNT's.

The G band of SWNT's lies at a somewhat higher frequency than quoted for metallic and semiconducting singlewalled nanotubes (see [9], Fig. 6). The width of the G band in the SWNT

sample is between  $40\text{ cm}^{-1}$  and  $75\text{ cm}^{-1}$  that appears to be close to the width of the  $G^+$  band, corresponding to atomic displacements along the tube axis [9] is remarkably different from the Breit-Wigner-Fano asymmetric and broad lower component ( $G^-$ ) in metallic nanotubes [9]. Thus the contribution of metallic nanotubes to the SWNT sample is probably small.

It is also instructive to examine the second-order  $G'$  band, in the MWNT sample which occurs at  $2724\text{ cm}^{-1}$  compared to that for SWNT which occurs at lower Raman shifts ( $2679\text{ cm}^{-1}$  -  $2689\text{ cm}^{-1}$ ). The shape of this band in the singlewalled bundles spectra could be fitted well to a Lorentzian form, as shown in Fig. 4 below.

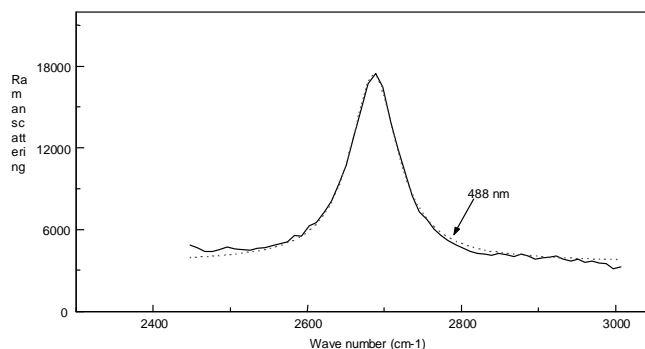


Fig. 4. Lorentzian fit to the  $G'$  band of SWNT bundle spectra, using the 488 nm Ar+ excitation line.

The corresponding  $G'$  band in MWNT spectra at  $2724\text{ cm}^{-1}$  is also well approximated by a Lorentzian form, as is seen in Fig. 1. It is known from the literature [10] that the  $G'$  band has a Lorentzian form in single wall CNT's, whereas in graphite it has low wave number shoulder, and that the frequency of the  $G'$  band should be very close to twice the frequency of the D band. In our case the D band for the SWNT bundles lies between  $1330\text{ cm}^{-1}$  and  $1390\text{ cm}^{-1}$ , thus  $G'$  is predicted to lie between  $2660\text{ cm}^{-1}$  and  $2780\text{ cm}^{-1}$ , the average of these limits coincides exactly with the measured  $G'$  band centre value.

### 3.2. Raman spectra of graphite and multiwalled nanotube samples

The Fig. 5 below is the Raman spectrum of the D and G bands of the graphite sample and also shows Lorentzian lineshape analysis of the features. The feature at  $1377.1\text{ cm}^{-1}$  is the D band due to amorphous carbon, while the weak  $1590.6\text{ cm}^{-1}$  component is the G band that predominates in highly crystalline graphite [3]. The intensity relationship between the D and G band in Fig. 5 indicates a low crystallinity of the graphite sample.

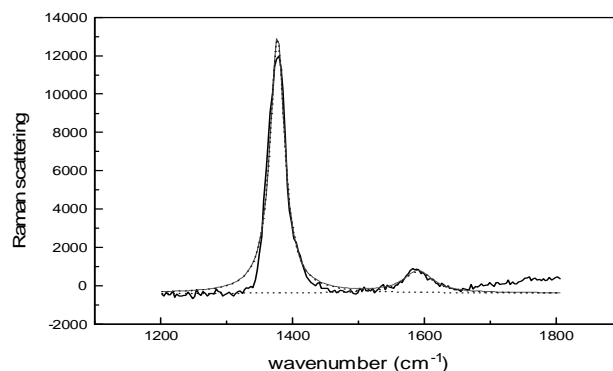


Fig. 5. is the Raman spectrum of the graphite sample taken with the 514.5 nm Ar+ laser line.

Fig. 1 shows the overall Raman spectrum of the multiwalled CNT sample. Here we give some more details for the various features in it. The Lorentzian analysis of the D/G band pair is shown in Fig. 6. for laser excitation wavelength 514.5 nm. The D and G band centre values are  $1364.6\text{ cm}^{-1}$  and  $1593.7$ , respectively for 514.5 nm excitation.

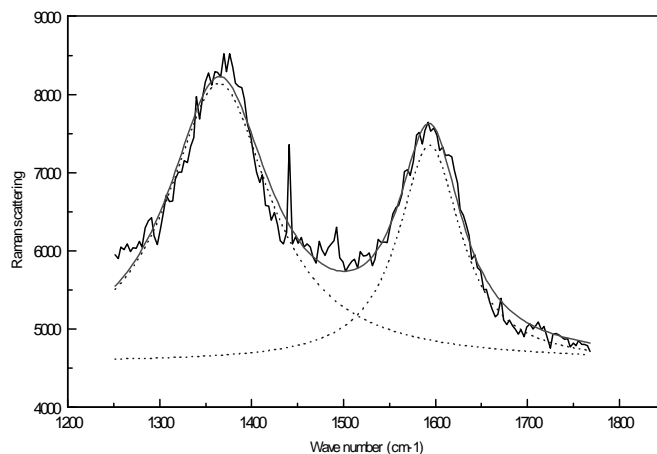


Fig. 6. Lorentzian analysis of the B/G band pair for the MWNT sample.

### 3.3. Microscopic studies of the samples

Morphological studies were also carried out on our CNT samples using scanning electron microscopy (SEM) for the SWNT, and scanning tunnelling microscopy (STM) for the MWNT samples. Fig.7 shows an SEM picture of the multiwalled sample.

The MWNT SEM picture in Fig. 7 shows thick bundles (of diameter approx. 30-40 nm) and, also some blobs of amorphous carbon. The thick feature in the SWNT STM picture is a bundle of many individual singlewalled CNT's but there are much narrower tubes also, the diameter of which is close to 4 nm. It is not excluded that these narrower features are also bundles of 2-3 SWNT's. There is no amorphous material seen in Fig. 8 where the background structure belongs to surface morphology of the HOPG graphite substrate.

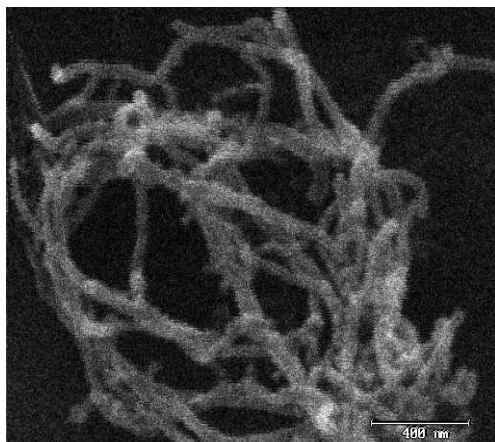


Fig. 7. SEM picture of the MWNT sample.

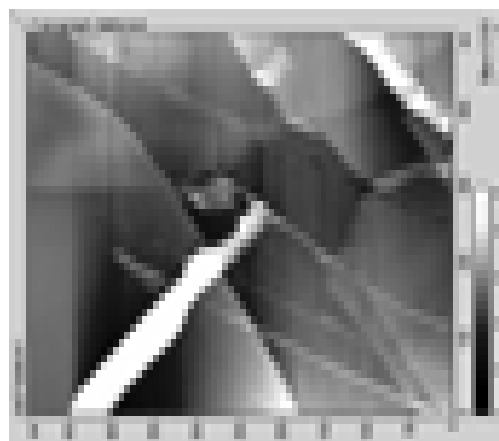


Fig. 8. STM picture of the SWMT sample.

#### 4. Conclusion

The Raman spectroscopic and microscopic studies reported here allowed us to characterize a multiwalled and a single walled carbon nanotube sample in terms of nanotube diameter and purity. This preliminary information will allow us to pursue more detailed spectroscopic research using Raman microscopy and surface-enhanced Raman spectroscopy. The slight dispersion of the Raman bands upon laser energy changes can be increased by using a broader range of excitation wavelengths, and also the anti-Stokes scattering in our future studies. This will make it possible to further identify weak components in Raman spectra.

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