Carbon NanoTubes– What information does Raman bring ?

Carbon NanoTubes (CNT) form a new class of materials that have attracted interest for a variety of engineering applications. Structurally they are related to graphitic carbon. One can conceptualise the structure of a Single-Walled Carbon Nanotube (SWNT) by imagining a single layer of graphite that is rolled into a tube (Figure 1). The orientation of the graphite plane relative to the axis of the tube, as well as the diameter of the tube, will determine many physical properties; tubes can be insulating, semiconducting, or metallic. When multiple layers of graphite are rolled into a single tube, the resulting structure is called a Multi-Walled Carbon Nanotube (MWNT).

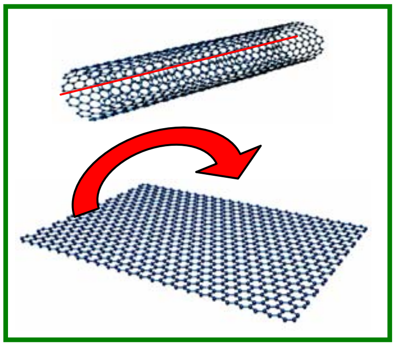


Fig.1: Illustration of the structure of a single walled carbon nanotube from a graphite sheet.

These materials have provided fertile ground for solid state calculations that predict the electronic and vibrational properties [1] of these structures. The large variety of SWNT's is defined by a pair of integers (n,m) from which their diameter, chirality (a parameter relating the orientation of the rolled graphite sheet relative to the main axis of the tube) and electronic behavior can be determined.

Raman spectra of these tubes are quite interesting because of resonance phenomena and sensitivity to tube structure. That is, there is <u>very</u> strong excitation wavelength dependence of the spectra resulting from the electronic band structure. In fact, the resonance Raman behavior in carbon nanotubes is unusual in that both the incident and the scattered photon have the possibility to resonate with the electronic excitations. For this reason the frequencies on the anti-Stokes side may not be the same as those on the Stokes side [13]. Because of this, the features in the Raman spectra are diagnostic of the CNT type [8].

There are limitless opportunities to take advantage of the tubes' properties in engineered materials. For instance, composites will take advantage of the tensile strength of the tubes and metallic tubes have already been used in integrated circuits [9].

The characteristic Raman spectrum of SWNT

The most important feature in the Raman spectrum of CNT's is the Radial Breathing Mode (RBM), which is often observed between 100 and 250 cm^{-1}. The frequency of the RBM (ω_r in cm^{-1}) is directly linked to the reciprocal of the nanotube diameter (d_t). In the case of an isolated SWNT this relation is [1]:

$$\omega_r = 224/d_t$$

However, non isolated SWNT's are subject to inter-tube interactions which increase the frequency of the RBM.

The D mode (the disorder band is well-known in disordered graphitic materials and located between 1330-1360 cm^{-1} when excited with a visible laser) is expected to be observed in Multi Walled NanoTubes (MWNT). However when it is observed in SWNT's, one assumes that it is due to defects in the tubes.

The G mode or (TM- Tangential Mode) corresponds to the stretching mode of the -C-C- bond in the graphite plane. This mode is located near 1580 cm^{-1}.

Exciting at several wavelengths- WHY ?

As mentioned earlier there is strong excitation wavelength dependence on the Raman intensity of SWNT's resulting from the proximity of the laser wavelength to the transitions between electronic states. The densities of states (DOS) which determine the transition energies and intensities can be calculated and are quite sensitive to the tube structure [1].

Each SWNT exhibits a Resonance Raman spectrum in a certain range of excitation wavelengths (i.e. when the excitation wavelength matches the energy gap between the DOS). Figure 2 shows the Kataura plot that correlates the frequency of the Raman shift of the RBM to the energy separation of the peaks in the DOS for each type of tube characterized by (n,m). In resonance conditions, the Raman signal is highly enhanced and it is even possible to record the Raman spectrum of an isolated Carbon Nanotube from which one can determine its structural and electronic properties (n,m) [4].
The RBM is the feature in the spectrum which is most characteristic of the structure of the tube. Consequently the Kataura plot summarizes all the information contained in the Raman spectrum.

When the Resonant Raman spectrum of one/several SWNT has been recorded, the Kataura plot allows one to determine its/their semiconducting or metallic behaviour, to estimate its/their diameter and (n,m) integers [4].

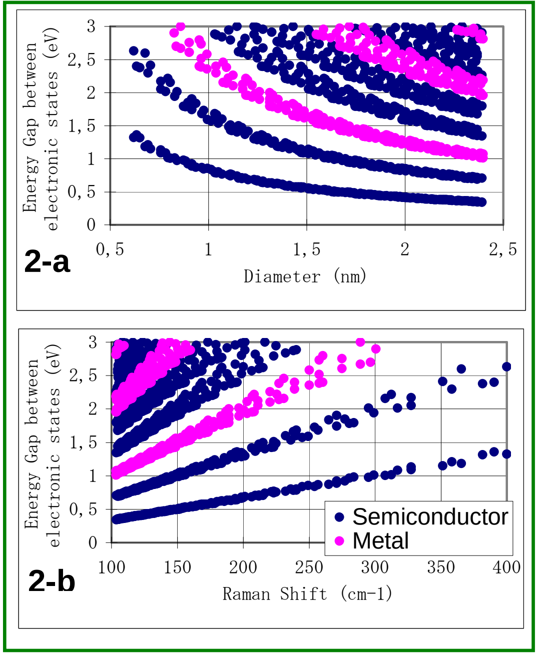


Fig.2: Kataura plots based on the energy of the C-C nearest neighbour interaction of 2.9eV – From Prof. Maruyama's home page [12]. The energy gaps between the electronic states is plotted as a function of the tube diameters (figure a) and Raman shift (figure b).

Exciting at several wavelengths allows one to select several resonance conditions in order to observe the existence of various species of Carbon Nanotubes in the sample. Figure 3 clearly demonstrates that this procedure is a good way to enhance selectively the Raman spectrum of different SWNT's [6].

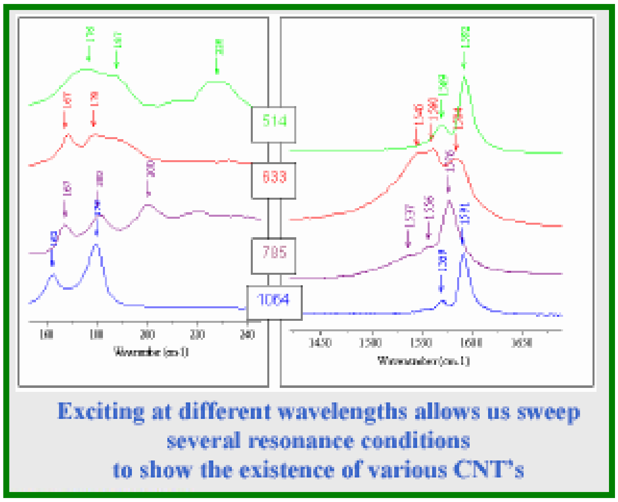


Fig.3: Spectra recorded at several wavelengths on the surface of a powder of SWNT's .

Need for spectral resolution- WHY ?

High Spectral Resolution is needed to separate very close modes in the spectrum of a single Carbon Nanotube or in the spectrum of a bundle of Carbon Nanotubes. Figure 4 shows a RBM spectrum that represents a collection of at least three different tubes in the laser focal volume.

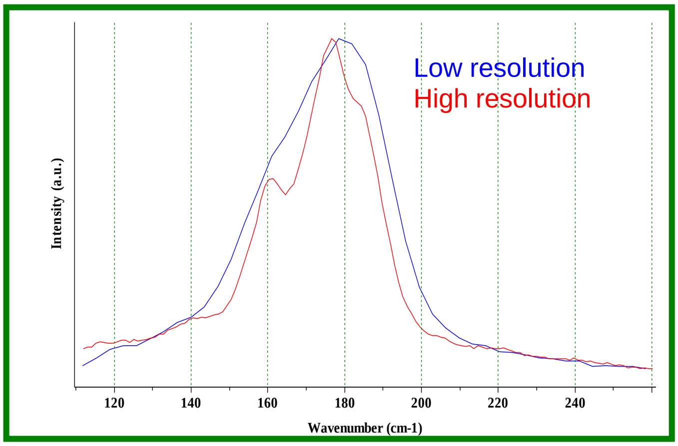


Fig.4: RBM Raman spectrum of a sample bundle of SWNT's LabRAM at 633nm.

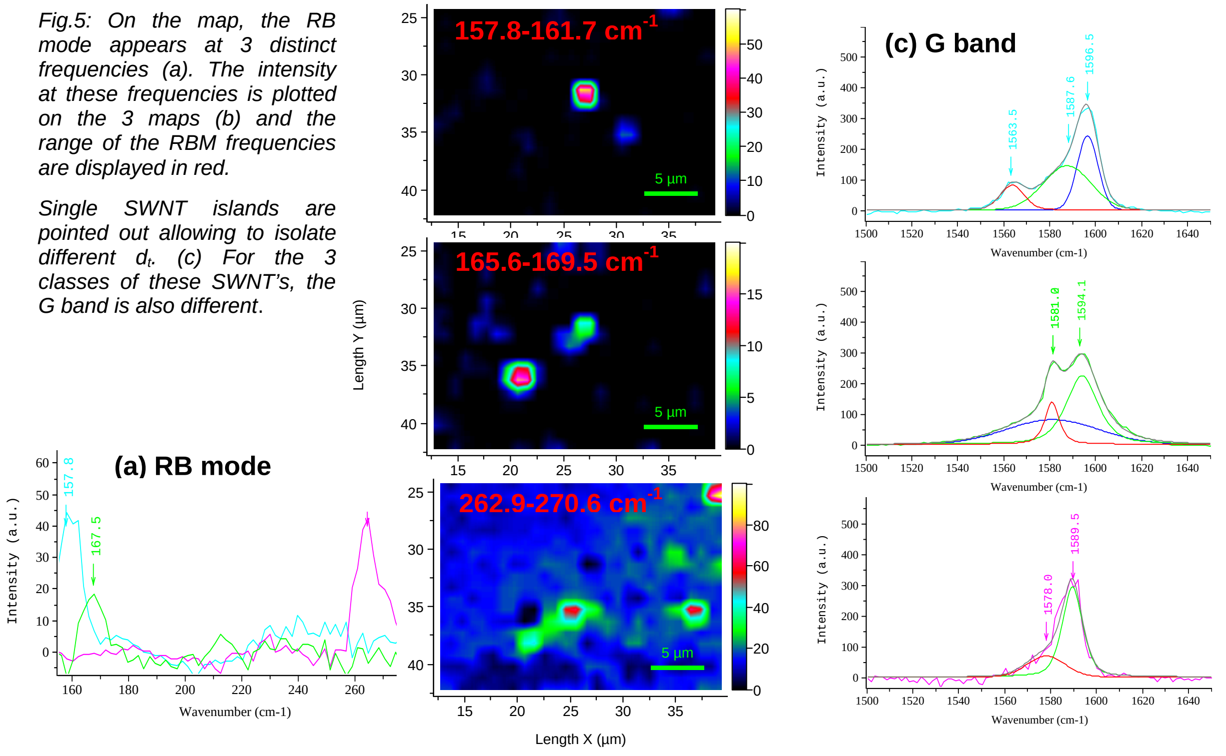
Need for spatial resolution- WHY ?

Using resonant conditions in Raman micro-spectroscopy, the spectrum of a single isolated SWNT can be detected. The difficulty for those experiments is to localise the nanotube on the surface. Probing a large area of the substrate by means of a map is often the only way to find the "hot spot" [2, 5].

In the map of Figure 5, three RBM frequencies positions are plotted revealing the distribution of the different tube diameters. From the RBM frequency one can estimate the tube diameter at each measurement point. The tubes in this work are scattered on a silicon substrate and are approximately 0.8nm to 1.5nm in diameter. Despite the fact that the laser spot is much larger than the tube diameter the resonance behaviour of the tubes allows the spectra to be recorded.

Fig.5: On the map, the RB mode appears at 3 distinct frequencies (a). The intensity at these frequencies is plotted on the 3 maps (b) and the range of the RBM frequencies are displayed in red.

Single SWNT islands are pointed out allowing to isolate different d_t. (c) For the 3 classes of these SWNT's, the G band is also different.



On Figure 6, a line measurement allows one to detect the Single-Walled Carbon Nanotubes connecting the source and drain electrodes of a CNT FET. The software (LabSpec) displays the image of the sample with the points of measurements (6-a), the series of spectra recorded along the line (6-b), one selected spectrum (6-c) and the intensity of selected peaks recorded as a function of position along the line (6-d).

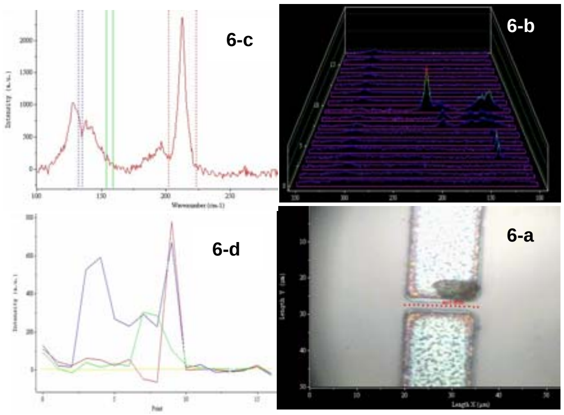


Fig.6 : Measurement performed at 633nm on a LabRAM HR Data courtesy of Prof. K. Matsumoto, The Institute of Scientific & Industrial Research, Osaka University, Japan.

The effect of increasing temperature

Since light absorption in nanotubes is high, there can be an increase in the temperature of the material which can sometimes cause changes in the sample. Therefore, it is necessary to monitor the effects of power density at the sample. Because the temperature changes in Carbon Nanotubes induce frequency down-shifts, temperature changes are easy to detect. The amplitude of the shift varies for each mode. For example, the G band follows a downshift of 0.026 $cm^{-1}.K^{-1}$ for a Multi-Walled NanoTube [1].

Measuring a spectrum first at low power density and then at high power density has been performed. Dramatic spectral changes occur when the laser power is increased and those modifications can be partially reversible. The effect is mainly due to a decrease in the quantity of defects, as shown in Figure 7; the D band clearly disappears during the heat treatment and does not recover (when the laser power is reduced, green spectrum). For samples that are particularly sensitive to laser power a line-scan feature can be employed in order to reduce the power density at the sample spot and also decrease the time required to map a sample.

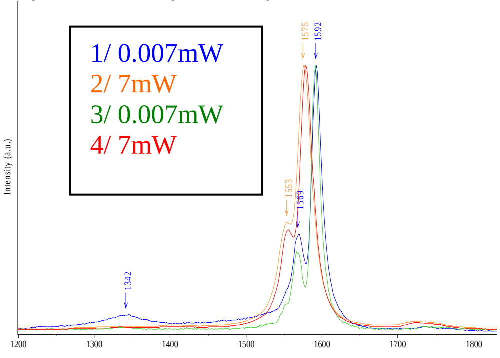


Fig.7 : All the spectra are recorded on the same point on a powder of SWNT's. Source 532nm. Objective 100x (NA= 0.9). Blue: spectrum recorded with a 0.007mW. Orange: spectrum recorded with a power of 7mW. Green: spectrum recorded at 0.007mW after a 30mn cooling. Red: spectrum recorded at 7mW.

Band gap Photo Luminescence / Fluorescence can be collected from SWCNT

In addition to Raman scattering, Photoluminescence emission of the excited sample can bring information on the Carbon Nanotubes' structure [10]. This new approach is revealed to be another tool to study the Carbon Nanotube chemical and physical properties which are affected by their structure.

The Fluorescence map displayed in Figure 8 shows the CNT's scattered on the surface that are not visible with standard optical microscopy, even at 100x magnification. The Fluorescence spectra show differences that allow one to differentiate several nanotube structures. [Note : a scale in cm^{-1} is commonly used to display Raman spectra whereas nm is more appropriate for PL results].

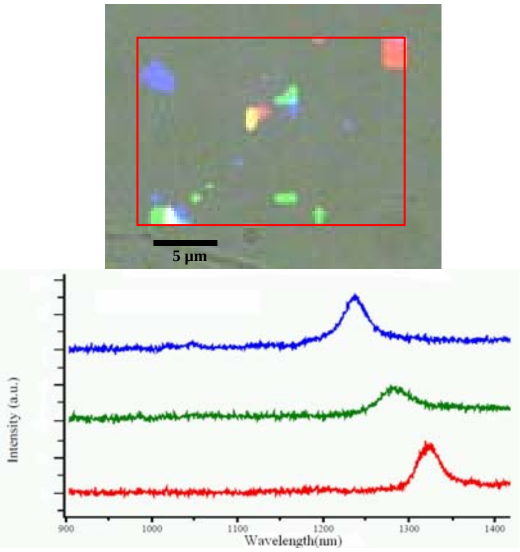


Fig.8: PL imaging for locating specific SWNT's dispersed on substrate. Excitation 785nm. Distribution of 3 characteristics Fluorescence spectra (red, blue, green). Data courtesy of Dr. H. Maki, Keio Univ., RIKEN Wako Institute, Japan.

Excitation wavelength dependence of photoluminescence spectra [11].

It has been shown by J.Lefebvre, et al. [11] that the photoluminescence intensity strongly depends on excitation wavelength. By changing the excitation wavelength it is possible to highlight PL peaks which are resonant.

Raman and PL imaging can be performed on the same area with the same instrument (see Figure 9). The correlation between the two intensity maps is good and the information obtained is complementary.

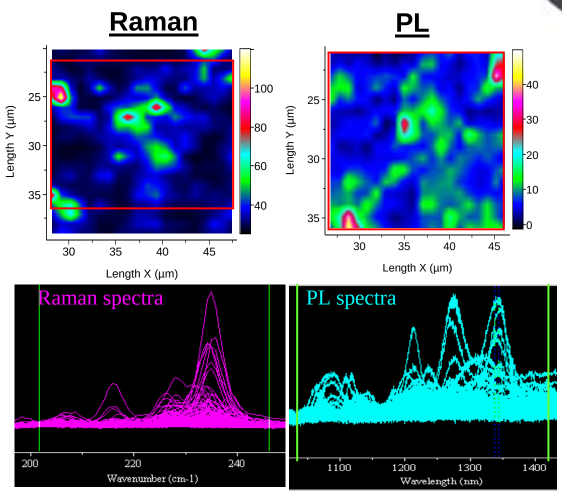


Fig.9: Raman and PL intensity maps of the same sample area. The correspondence between the PL map boundaries and the Raman map is given by the red square. The green cursors define the zone of interest in the spectra. Scale in cm^{-1} is commonly used for Raman whereas nm is more appropriate for PL results. Data courtesy of Dr. H. Maki, Keio Univ., RIKEN Wako Institute, Japan.

Conclusion:

This note demonstrates that depending on the configuration of the Raman system used, one can extract different types of information about Carbon Nanotubes. A multi-excitation, low frequency, high spectral and spatial resolution Raman system is the best solution to collect the maximum of information.

Raman has shown a high potential in characterising the Single-Walled Carbon Nanotubes' structure. The correlation between knowledge about structure with physical and chemical properties about the tubes make the technique extremely powerful to control the quality of the Single-Walled Carbon Nanotubes for specific applications.

Clearly instrument capabilities, including high spatial resolution, high spectral resolution, and flexibility in excitation wavelength, enhance the potential to derive information from the Raman spectra of Carbon Nanotubes.

With the addition of a NIR detector PhotoLuminescence and Raman phenomena can be detected on the same instrument and allow the correlation of information about a specific sample of Carbon Nanotubes.

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HORIBA JOBIN YVON

France : HORIBA Jobin Yvon S.A.S., 231 rue de Lille, 59650 Villeneuve d'Ascq. Tel : +33 (0)3 20 59 18 00, Fax : +33 (0)3 20 59 18 08. Email : raman@jobinyvon.fr www.jobinyvon.fr
USA : HORIBA Jobin Yvon Inc., 3880 Park Avenue, Edison, NJ 08820-3012. Tel : +1-732-494-8660, Fax : +1-732-549-2571. Email : raman@jobinyvon.com www.jobinyvon.com
Japan : HORIBA Ltd., JY Optical Sales Dept., 1-7-8 Higashi-kanda, Chiyoda-ku, Tokyo 101-0031. Tel: +81 (0)3 3861 8231, Fax: +81 (0)3 3861 8259. Email: raman@horiba.com
Germany: +49 (0) 6251 84 75-0 **Italy:** +39 02 57603050 **UK:** +44 (0)20 8204 8142
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