Abstract
Carbon Nano Tubes (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).

Keywords
Raman Spectroscopy, nanotechnology characterization, SWNT, CNT, Ultra Low Frequency (ULF)

The large variety of SWNTs is defined by a pair of integers \((n,m)\) from which their diameter, Chirality and Semiconducting / metallic behaviour can be determined. Chirality defines the orientation of the rolled Graphite sheet relative to the main axis of the tube.

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 (\(\omega_\text{r} \text{ cm}^{-1}\)) is directly linked to the reciprocal of the nanotube diameter (\(d_t\)). In the case of an isolated Single Wall NanoTube (SWNT) this relation is [1]:

\[
\omega_\text{r} = \frac{224}{d_t}
\]

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 Wall 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 \(-\text{C-C-}\) 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 (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 3 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 (n,m) properties.

The semiconducting nanotubes generally have resonance between 457.9 nm (2.7 eV) and 514.5 nm (2.4 eV) and at 1064 nm (1.17 eV) whereas the metallic nanotubes have resonance in the UV (< 3 eV) and around 1064 nm. 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 (n,m) properties.

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/these semiconducting or metallic behaviour, to estimate its/these diameter and (n,m) integers.
There is currently no way to synthesize selectively one kind of SWNT with a fixed diameter \(d\) and orientation \((n,m)\). Exciting at several wavelengths allows to sweep several resonance conditions in order to point out selectively the existence of various carbon nanotubes in the sample. Figure 4 clearly demonstrates that this procedure is a good way to enhance selectively the Raman spectrum of different SWNTs [6].

Need of spectral resolution- WHY ?

High Spectral Resolution is needed to separate very close modes in the spectrum of a single nanotube or in the spectrum of a bundle of nanotubes. Figure 5 shows a RBM spectrum that represents tubes with at least 3 different properties:

Need of 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 the mean of a map is often the only way to find the “hot spot” [2, 5].

The effect of increasing temperature

The light absorption coefficient of the sample depends on the wavelength of the excitation source. If the light absorption coefficient is high, this may lead to an increase of the temperature in the material and sometimes to damage of the sample. Therefore, it is necessary to reduce the power density at the sample. It is very easy to monitor whether a frequency shift occurs. The temperature changes in carbon nanotube induce frequency down shifts. The amplitude of the shift varies for each mode. For example, the G band follows a downshift of 0.026 cm\(^{-1}\).K\(^{-1}\) in a MultiWall NanoTube.

An experiment has been performed by measuring a spectrum first at low power density and then at high power density. Dramatic spectral changes occur when the laser power increases 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 after the heat treatment. For samples that are particularly sensitive to laser power a line-scan feature can be employed. This feature can also be employed to decrease the time required to map a sample.
Band gap Photo Luminescence / Fluorescence can be collected from SWCNT

In addition to Raman diffusion, Photoluminescence emission of the excited sample can bring information on the Nanotubes’ structure [10]. Figure 8 shows the principle of Band gap Photoluminescence / Fluorescence using the typical density of state diagram already displayed figure 2.

This new approach is revealed to be a complementary tool to study the nanotube chemical and physical properties which are affected by their structure.

![Schematic density of electronic states for a single nanotube structure. Solid arrows depict the optical excitation and emission transitions of interest; dashed arrows denote nonradiative relaxation of the electron (in conduction band) and hole (in valence band) prior to emission – from ref 10.](image)

Fig. 8: Schematic density of electronic states for a single nanotube structure. Solid arrows depict the optical excitation and emission transitions of interest; dashed arrows denote nonradiative relaxation of the electron (in conduction band) and hole (in valence band) prior to emission – from ref 10.

Excitation wavelength dependence of photoluminescence spectra

![Excitation wavelength dependence of photoluminescence spectra.](image)

Figure 9: J. Lefebvre, Y. Homma, and P. Finnie, Phys. Lett. 90, 217401, (2003). Photoluminescence spectra are shown for a series of excitation wavelength. Spectra were taken at room temperature in air using various lasers. A 100μm spot diameter and an average power of 1.7mW was used in all cases. Each spectrum is offset along the y axis by an amount proportional to the excitation wavelength. The same laser power and collection optics were used for all spectra so the intensity can be compared for different curves. The thick gray band highlights the expected PL resonance. The black vertical lines highlight PL peaks which are resonant. The dotted and dashed lines trace the G’ and G Raman modes, respectively.

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 multieexcitation, low frequency, high spectral and spatial resolution Raman system is the best solution to collect the maximum information.

Raman has shown a high potential in characterising the SWCNTs’ 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 SWCNTs for specific applications. Raman spectrometer capabilities like spatial resolution, spectral resolution and excitation wavelength versatility have been examined. Beside Raman, preliminary fluorescence studies are describing the potential of the technique.

Reference

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