

NE 226 L

Characterization of Materials

Title Page

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1. Introduction

Raman spectroscopy is quite similar to FTIR except Raman can detect vibrational modes corresponding to symmetric stretches that do not cause a dipole moment. The spectroscopic method shines light through a sample and records the *scattered* radiation from the sample. There are two types of scattering: elastic (Rayleigh) and inelastic (Raman). The latter occurs when there is an exchange of energy between the incident photon and the molecule. If the molecule gains energy after the collision, the transition is referred to as Stokes transitions; if the molecule loses energy, the transition is referred to as anti-Stokes transitions.

The basic set-up of a Raman spectrometer is shown in Figure 1. The detector is always placed perpendicular to the direction of the incident radiation so as to observe only the scattered light.

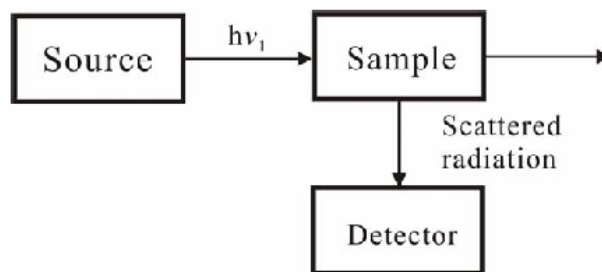


Figure 1 Basic set-up of a Raman spectrometer

The criteria for a molecule to be Raman active are given by a set of gross selection rules. Unlike FTIR, the molecule need not have to possess a permanent dipole; rather it is the *polarizability* α of the molecule that determines if it will be Raman active. The strength of the induced dipole as well as the energy of the interaction are both proportional to α . More importantly, Raman scattering only occurs if the polarizability of the molecule varies with orientation. Two types of Raman spectroscopy are possible: rotational and vibrational. The type of transition is determined by the energy of the incident radiation as rotational transitions typically occur at lower energies than vibrational transitions.

Raman spectroscopy is useful to determine bond-lengths, especially in non-polar molecules. It can also be used to fingerprint and therefore determine identity of organic and inorganic species in solution. Raman spectroscopy is therefore used primarily as a *structural* characterization technique more than anything else.

2. Materials and Methods

The instrument used in this experiment was a SENTERRA Raman Spectrometer manufactured by Bruker Optics GmbH. The material to be analyzed is a single walled

carbon nanotube (SWNT). The experimental procedure to operate the SENTERRA is outlined in the lab manual of *Characterization of Materials* [1], under experiment number 2. The SENTERRA Raman spectrometer includes two lasers and also a simple confocal microscope. Typically, samples are observed using the optical microscope before being subjected to a Raman analysis. The visual observation is useful because it reveals various morphological details within a sample such as colour, size, and shape. These physical details coupled with the information about molecular structure gleaned from the Raman analysis makes the Raman spectroscopic method indispensable for materials characterization.

3. Results

The spectrum obtained by analyzing a single walled carbon nanotube with a Raman spectrometer is attached. The output is a plot of the Raman intensity vs. the radial breathing modes (RBMs).

4. Discussion

The radial breathing mode (RBM) which appears in the low frequency region (100 – 400 cm^{-1}) in a Raman spectrum is one of the most important vibrational modes of single walled carbon nanotubes (SWNTs). This mode has a much stronger dependency on the diameter of the nanotube than other vibrational modes.

The diameter of the nanotube can be determined within an accuracy of one angstrom:

$$\nu_{RBM} (\text{cm}^{-1}) = \frac{223.5}{d_t (\text{nm})} + 12.5$$

From the above equation, we can solve for d_t in terms of ν to obtain:

$$d_t (\text{nm}) = \frac{223.5}{\nu_{RBM} (\text{cm}^{-1}) - 12.5}$$

The frequencies corresponding to the radial breathing modes in the low frequency region (100 – 400 cm^{-1}) and their respective diameters are summarized in the following table.

$\nu (\text{cm}^{-1})$	$d_t (\text{nm})$
206.73	1.15
229.50	1.03
266.05	0.88

There are therefore on average nanotubes of three different diameters judging from the fact that three peaks were observed in the Raman spectrum.

5. Conclusions

The Raman spectrum showed us that our sample contained single walled nanotubes of *three* different diameters.

The average diameter (assuming the intensities of all three peaks are identical)

$$\text{is } \frac{1.15 + 1.03 + 0.88}{3} = 1.02 \text{ nm} .$$

6. References

- [1] Q. Xie, F. McCourt, *Nanotechnology Engineering NE 226 Lab Manual*, University of Waterloo, Waterloo, pp 28-34 (2007).
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