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A low-cost Raman spectrometer design used to study Raman scattering from a single-walled carbon nanotube[¶]

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Abstract. The paper discusses the design of a low cost Raman spectrometer. Single-walled nanotubes (SWNT) have been studied to demonstrate the reach of such a system. We observe both the radial-breathing mode (RBM) and the tangential mode from the SWNT. The tube diameters of the SWNT used in these experiments have been determined using RBM to be predominantly 1·4 and 1·6 nm. These are consistent with the TEM images taken of the same sample. The new method of producing SWNT using Ni–Y catalyst in electric-arc discharge method produces nanotubes with very small dispersion in diameter and high yields. The chirality of the SWNT can be deduced from their radial breathing modes, and it suggests that they are metallic in nature.

Keywords. Raman spectrometer; single-walled nanotubes; radial-breathing mode; chirality.

1. Introduction

Raman spectroscopy has over the past few decades been extensively used to study materials, especially, nano-materials. Raman spectroscopy can be obtained as a function of temperature and pressure, the two thermodynamic variables, with great ease. Over the years, there has been a lot of modernisation in the Raman spectrometer. The advent of lasers in the 1960's brought Raman spectroscopy to the forefront. The use of charge coupled device (CCD) detectors has made Raman measurements extremely simple. Over the years, Raman instrumentation has undergone a lot of changes, especially monochromators. Raman spectrometers have single, double and even triple monochromators to study very weak as well as low frequency Raman modes. The cost of these spectrometers has been a reason for worry. In this article we have designed a low cost and flexible Raman spectrometer, which is based on a single monochromator and a CCD detector, coupled to a custom-built microscope using a fibre optic cable. To demonstrate the range of this instrument we have studied single-walled nanotubes (SWNT).

SWNT constitute a new form of carbon allotropes with unique physical properties. SWNT can be metals with conductivity comparable to that of copper and mechanical strength exceeding that of diamond. They are also excellent thermal conductors with variable gaps (0–1 eV).[1–3] The unique properties of the SWNT arise from their one-

[¶]Dedicated to Professor C N R Rao on his 70th birthday
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dimensional structure and these give distinctive Raman bands. Raman scattering on SWNT has been studied intensively in the literature.[4–10] Raman spectrum of the SWNT has mainly two parts: (a) A_{1g} radial breathing mode (RBM) ~ 100–300 cm^{-1} and (b) unresolved triplet (A_{1g}, E_{1g} and E_{2g}) tangential C–C stretching mode (TM) ~ 1450–1650 cm^{-1}. The Raman frequency of the RBM is directly related to the diameter of the SWNT, whereas the TM provides the insight into the electronic properties of the nanotubes.[8–10] There is also a weak intermediate frequency region ~ 300–1400 cm^{-1}, which is related to the chirality of the SWNT. The Raman peaks of SWNT's are inhomogenously broadened due to the inherent tube diameter distribution present in the material.

The frequency of the A_{1g} symmetry RBM, in which all the carbon atoms undergo an equal radial displacement, is strongly diameter-dependent and hence is used to measure the tube diameter.[4] An empirical expression for the RBM frequency (ν_r) is given by

$$\nu_r = 223{\cdot}75/d, \tag{1}$$

where ν_r is measured in wave numbers and d is measured in nanometres. This is independent of the chirality.

SWNT can be constructed by wrapping a single sheet of graphene. The wrapping or the chiral vector $n\mathbf{a}_1 + m\mathbf{a}_2$, or ($n$, m), where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors in the 2-D graphene sheet and n and m are integers, determines the symmetry of the SWNT.[1,11] This leads to three types of nanotubes depending on the values of n and m: the armchair nanotubes where $n = m$, zig-zag nanotubes where $m = 0$, and chiral nanotubes where $n \neq m \neq 0$. A nanotube is metallic when $n - m$ is divisible by 3; otherwise it is semiconducting. The diameter of the nanotube is related to the (n, m) values by,[11]

$$d = a(n^2 + m^2 + nm)^{(1/2)}/\pi, \tag{2}$$

where the lattice constant on a graphene sheet a is taken to be 2·49 Å on a rolled up nanotube cylinder.[1]

In the present work, we have carried out Raman scattering studies on SWNT prepared by electric-arc discharge method. We find that the SWNT samples have tube diameters of 1·57 and 1·76 nm and their chiral vectors are (13, 10) and (18, 6) respectively. This suggests that the SWNT samples in the present investigation are metallic.

2. Experimental details

Figure 1 shows a schematic diagram of the recently designed Raman spectrometer used in the present investigations. The heart of the system is a Jobin Yvon Triax 550 with triple grating used as the monochromator. Detection of Raman signals is done by 1024 × 256 back thinned liquid N_2 cooled CCD detector. The Raman signals are collected by a microscope objective with long working-distance as well as a large numerical aperture. The objective used is Olympus, Japan make. A custom microscope has been built to view as well as to focus the collected scattered light to the single optical fibre (~ 100 μm) using the trinocular (Olympus, Japan). A super notch plus filter (Keiser Optics, USA) corresponding to the excitation frequency is introduced between the focusing lens and the optical fibre to cut the Rayleigh light from going into the fibre. The optical fibre is f-number matched with the spectrometer using a novel mirror based optical fibre coupler mounted on the Triax 550. The mirror arrangement takes care of any chromatic aberations.

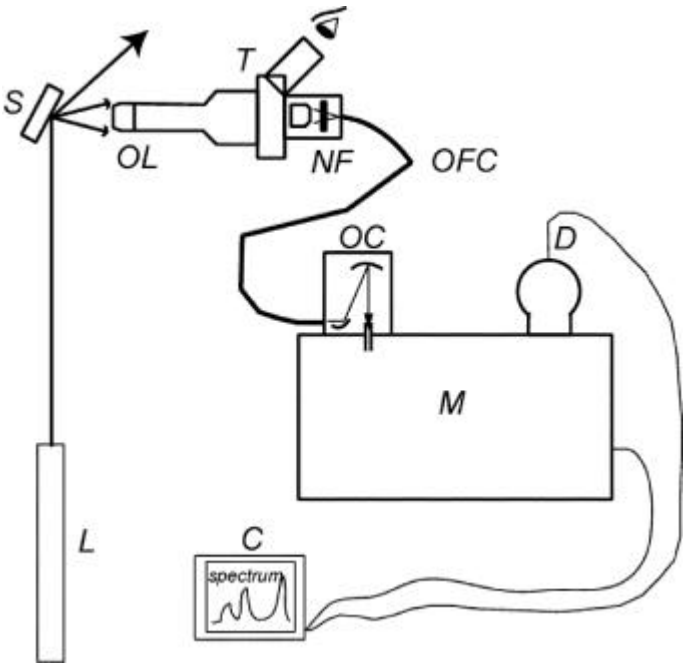

Figure 1. Schematic representation of the Raman spectrometer used in the present experiment. S – sample, L – laser, OL – objective lens, T – trinocular, NF – notch filter, OFC – optical fibre cable, D – CCD detector, OC – optical fibre coupling, M – monochromator and C – computer.

A solid state diode pumped Nd–YAG laser (Coherent Inc., USA) with excitation frequency of 532 nm was used. The two modifications in this set up done by us are use of mirrors to *f*-number match the fibre to the monochromator and use of tilt alignment for the notch filter. In principle, 0° notch filters should have a sharp cut off for the excitation frequency. But this is not the case, hence it is difficult to get Raman modes close to the excitation frequency. By tilting the notch filter angle, one can get Raman signals as close as 10 cm^{-1} to the excitation frequency. At present, we have been routinely recording Raman signals close to 50 cm^{-1}. With better control over the tilt alignment one can record very low energy Raman signals. The cost of such a system is nearly 1/3 of the commercially available models.

Single-shell nanotubes were first made by the electric-arc discharge method through the introduction of catalyst species along with the evaporated carbon. In the present case, a hole is drilled in the centre of the anode and packed with mixtures of metal catalyst and graphite powder, the metal being 1–10% by weight. Several catalysts have been used but the best yield of nanotubes has been obtained for Co, Ni and bimetallic systems such as Co–Ni, Co–Pt and Ni–Y. During the arc discharge web-like structures are formed and decorated the colder electrode parts and the outer regions of reaction vessel. These contain large amounts of bundles containing 10–100 single-shell nanotubes co-deposited along with amorphous carbon and nanoparticles of the catalyst particles. Originally, the amount of single shell material that could be produced were small, less than microgram quantities. More over, the samples were contaminated from amorphous carbon and small

amount of catalyst particles. Very recently, the use of a Ni–Y catalyst in the arc-discharge has provided very good yields (< 75%) of single shell nanotube material.

The Raman measurements were done in 90° geometry, with a spectrometer resolution of around 1–2 cm^{-1} and laser powers of less than 20 to 30 mW on the sample. Typical recording times were around 180 to 600 s. The spectrum was calibrated using neon lamp excitations.

3. Results and discussion

Figure 2 shows the room temperature Raman spectrum of the SWNT in the frequency range 50–1700 cm^{-1}. We carried out the polarisation dependence of the Raman bands. We find no significant change in the intensities or the modes. The random orientation of the nanotubes in our sample could be the possible reason for such a behaviour. The strongest features are found around 100–200 cm^{-1} and 1400–1700 cm^{-1}. In the range 300 to 1400 cm^{-1} there are many weak peaks found. We would be concentrating on only the strong features. In the RBM region we see two distinct peaks in the spectrum. We can thus infer that we have at the least two diameter sizes of nanotube, with a distribution around them. This is corroborated in the high frequency Raman band (1400–1700 cm^{-1}), where also we find two peaks. The energy of the laser excitation used in our experiment is 2·33 eV. It has been seen that in this range of energies the Raman bands do not show any resonance behaviour.[12]

Figure 3 shows the fitting of the Raman modes in the range 100–200 cm^{-1} by a sum of Lorentzian lines. At the least 3 different peaks were necessary to give a good fit to the experimental data and their frequencies are 140, 154 and 161 cm^{-1}. The average full-width at half maxima (FWHM) was found to be around 15 cm^{-1}. Similarly, figure 4

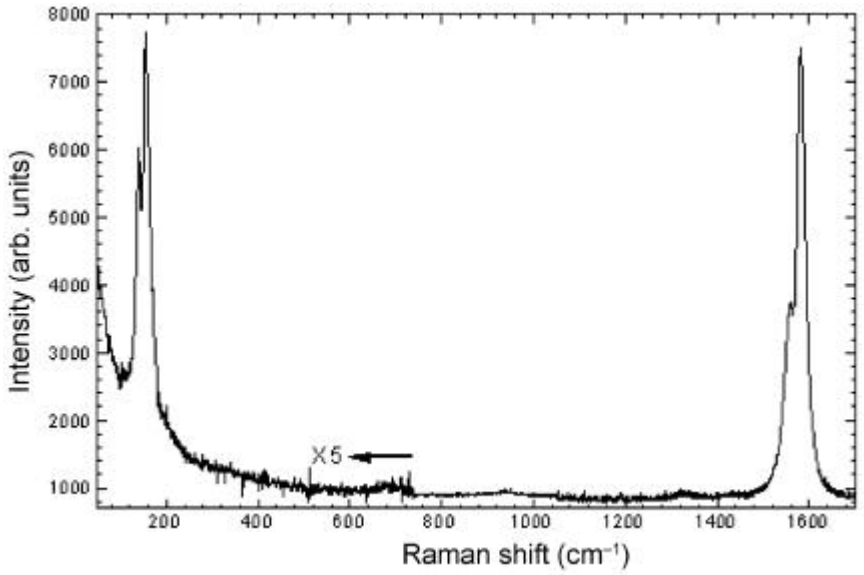

Figure 2. Room temperature Raman spectrum of the single-walled nanotube. The intensity of the low frequency region below 700 cm^{-1} has been multiplied by 5.

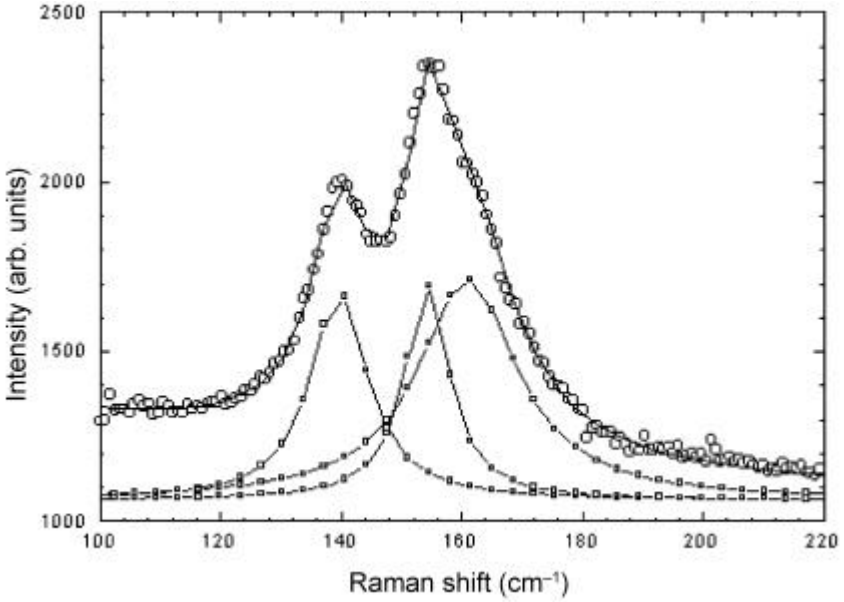

Figure 3. Radial breathing modes in the region of 100 to 220 cm^{-1}. The lines with square symbols are the Lorentzian fits to the data shown in open circles. The solid line through the data shows the convoluted spectrum.

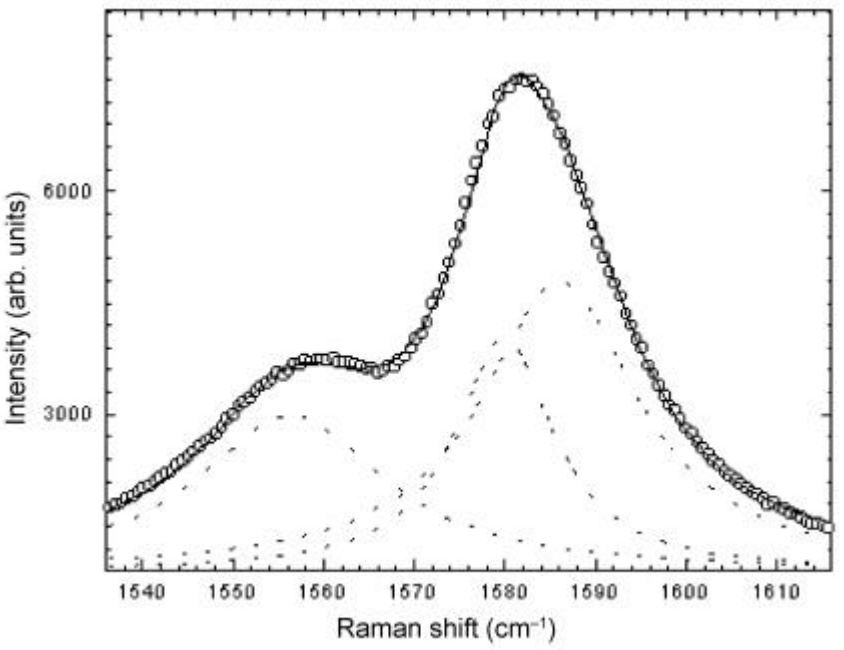

Figure 4. Tangential C–C stretching mode in the region of 1400 to 1700 cm^{-1}. The individual Lorentzian fits to the data (open circles) are shown by dashed lines. The solid line through the data shows the convoluted spectrum.

shows the fitting of the Raman bands in the high frequency region of 1400–1700 cm^{-1} by a sum of three Lorentzian lines. Their frequencies are 1556, 1580 and 1586 cm^{-1}. The average FWHM for the TM mode is 20 cm^{-1}.

Using (1) we can calculate the diameter of the SWNT in the given sample. The diameters are in the range of 1·4 to 1·6 nm. The average distribution around each tube diameters is 0·1 nm. TEM analysis of the same samples is consistent with these results. It has been seen that one can find the chirality hence the structure of one-dimensional systems, such as SWNT, using Raman spectroscopy.[13] The theory of resonant transitions is used to determine the (n, m) in the SWNT system. Using either the (2) or using table 1 of ref. [13], it is possible to say that the chirality associates with the present SWNT sample are (18, 6), (16, 7) and (14, 8) for 1·4, 1·45 and 1·6 nm tube diameters, respectively. It is also clear that from the criteria of metallic nanotubes (namely, $n - m$ is divisible by 3), that the present sample is metallic.

In conclusion, the design of the Raman spectrometer presented in this paper is comparable in performance to commercially available spectrometers. Raman results on the SWNT suggest that their size distribution is in a small range of 1·4 to 1·6 nm and that they have very few impurities, implying that the present method of preparing the nanotubes using Ni–Y catalysts products SWNT of relatively uniform size and high purity. The nanotubes thus produced are mostly metallic in nature. Finally, Raman spectroscopy provides an effective tool to study the structures of one-dimensional systems, such as carbon nanotubes.

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