

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231236003>

UV Raman Spectroscopy of Single-Walled Carbon Nanotubes

ARTICLE in CHEMISTRY OF MATERIALS · OCTOBER 2001

Impact Factor: 8.35 · DOI: 10.1021/cm0103186

CITATIONS

20

READS

36

3 AUTHORS, INCLUDING:



Ravindran Thoguluva

Indira Gandhi Centre for Atomic Research

118 PUBLICATIONS **965** CITATIONS

SEE PROFILE



John V Badding

Pennsylvania State University

189 PUBLICATIONS **2,596** CITATIONS

SEE PROFILE

Raman Spectroscopy on Single-Walled Carbon Nanotubes

Abstract:

Raman spectroscopy, a technique which observes the energies of vibrational transitions in molecules, is a useful tool for studying carbon nanotubes, which are hollow cylinders of nanoscale diameter composed of carbon. Raman spectroscopy measures the difference in energy between a source and the light scattered off of a sample. This energy difference corresponds to vibrational transitions in the molecules, specifically vibrations which change the polarizability of the molecules. Raman spectroscopy has many advantages over other methods of studying carbon nanotubes, and been applied to study nanotubes in many ways. Raman spectra can be used to distinguish between different types of nanotubes. The Raman peaks of nanotubes are sensitive to the surroundings of the nanotubes, pressure, temperature, and other parameters, leading to many different possible ways to use Raman spectroscopy in the study of nanotubes. An overview and specific examples of these types of studies are presented here.

Introduction

When radiation hits a molecule, many things could happen. Depending on the molecule and wavelength, much of the radiation may be absorbed and emitted in various ways. A small fraction of the radiation is scattered, most of it at the same wavelength as the incoming radiation (Rayleigh scattering). A very small fraction of the incoming radiation is scattered at a different wavelength due to Raman scattering. The difference in energy corresponds to vibrational transitions in the molecule. Infrared spectrometry is another way to observe the vibrational transitions, in which light of the energy of the transition is absorbed by the molecule. However, Raman spectroscopy has important advantages over infrared spectrometry in certain situations.

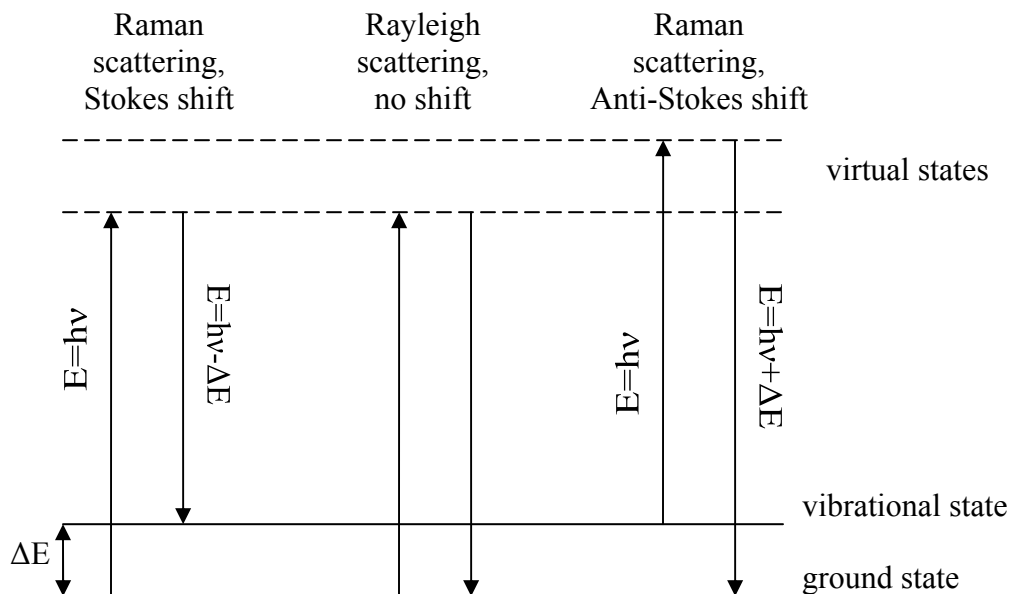
Since the signal is relatively small (about 0.001% of the incoming radiation), the source used must be powerful, and is often a laser.⁵ The wavelength of the source is not the important parameter, as it is in infrared spectrometry. Instead, the change in frequency of the scattered light, or the Raman shift, is the important information. This means that glass cuvettes can be used to hold the sample. With infrared spectrometry, glass might absorb light at frequencies which correspond to important parts of the spectrum, but Raman can use much higher frequencies which are not absorbed by glass. Other advantages of Raman scattering over infrared absorption is that water can be used as the solvent for Raman measurements and different peaks may be seen on the Raman spectra.⁵

The process of Raman scattering is shown in Figure 1. When a photon of radiation impinges on a molecule, it is absorbed, bringing the molecule to a virtual state,

which does not necessarily correspond to any particular electronic or vibrational states.

This is why Raman works with different source wavelengths.

Figure 1: Shifts in scattered radiation⁵

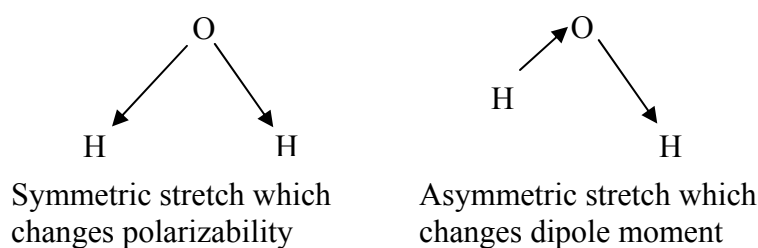


The energy is almost immediately released as a new photon, usually at the same wavelength as the incoming light. However, if the energy was absorbed from the ground vibrational state, but leaves the particle in a higher vibrational state, the scattered light will have a Stokes shift from the original light, as shown on Figure 1. As shown, an Anti-Stokes shift can occur if the molecule was in an excited vibrational state before absorbing the energy, but these shifts are less likely because of the small probability of finding a molecule in an excited vibrational state. The intensity of Anti-Stokes lines on a Raman spectrum goes up as the temperature is increased because this increases the number of molecules in an excited vibrational state.⁴

Raman lines correspond to vibrations which change the polarizability, unlike infrared absorption lines, which are due to a change in dipole moment. Figure 2 shows two vibrations of water. The symmetric stretch changes how far the hydrogens are from

the oxygen, impeding the molecule's ability to move charge around, so the polarizability is changed and this mode will be Raman active. The asymmetric stretch, however, brings one hydrogen closer while the other is farther from the oxygen, so that the total polarizability is unchanged, but the dipole moment is affected--this vibrational transition will be seen in an infrared absorption spectrum, but not in a Raman spectrum.⁵

Figure 2: Examples of Vibrations Changing Polarizability, Dipole Moment



Carbon nanotubes are like rolled-up sheets of graphite, so they are fairly symmetrical. Since they are composed entirely of carbon atoms, it is hard to imagine modes of vibration which significantly change the dipole moment. However, modes which bring the carbons farther apart or closer together change the polarizability, so carbon nanotubes are a good candidate for study with Raman spectroscopy. A sheet of graphite can be thought of as a honeycomb pattern of carbon atoms. If you cut out a rectangular box of the sheet and roll it into a cylinder, you will have a carbon nanotube. Depending on the angle that the rectangle is with respect to the axes of the honeycomb, different types of nanotubes can be formed. The nanotubes are characterized by their roll-up vector (n,m) , as shown on Figure 3, taken from I. Loa's paper². Naturally, different nanotubes will have different Raman spectra.

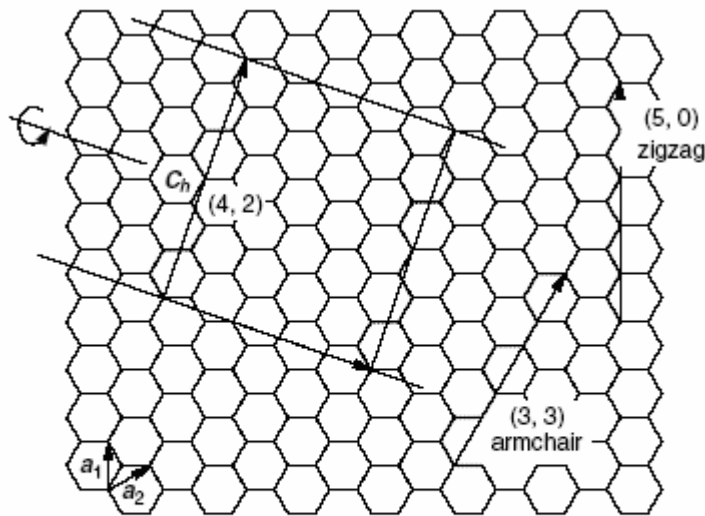


Figure 3. Rolling-up of a graphene sheet into a nanotube. The geometry of a single-wall nanotube is defined by the roll-up vector (n, m) or, equivalently, the chiral vector $C_h = na_1 + ma_2$. The chiral vectors of a zigzag and an armchair tube are also shown. **Copied from I. Loa, reference 2**

The first carbon nanotubes that were discovered, in 1991, were multi-walled carbon nanotubes (MWNTs), which are like several individual nanotubes fitted inside each other. Single-walled carbon nanotubes (SWNTs) were discovered in 1993, and since then have been the subject of much recent research. SWNTs have an extraordinarily high strength to weight ratio, interesting electrical properties, and many potential applications. They have such a small diameter that they can act almost as a one-dimensional electronic system. SWNTs can be metallic, semi-metallic, or semiconducting, depending on the roll-up vector.²

Methods and Analysis

Understanding the current data gathered on carbon nanotubes from Raman spectroscopy requires a deeper explanation of Raman spectroscopy in general. A basic knowledge of specific techniques, especially resonance Raman spectroscopy and surface-

enhanced Raman spectroscopy, is required. Resonance Raman spectroscopy is frequently used for carbon nanotubes to enhance the signal. Surface-enhancement has only relatively recently been applied for use on nanotubes, but it is gaining popularity.

The basic components of a Raman spectrometer are a source, a sample, and a detector. The source is often a near-infrared laser, such as a Diode laser or Niobium YAG laser.⁵ Liquid samples may be dissolved in many solvents, including water, as water's Raman peaks are small. Solid samples, such as polymers, can be used, and are often ground into a powder before the spectrum is taken. Because the Raleigh scattering line is so much more intense than the Raman lines, a notch filter, which filters a very small range of wavelengths, is often used after the sample.⁵ The instrument might have a grating to select a wavelength before the detector and then scan through the wavelength range over time, or it may have a detector that collects many frequencies at one time and decomposes them using a Fourier transform. Some instruments measure the depolarization ratio, defined as the intensity of perpendicularly polarized light divided by the intensity of parallel polarized light collected, where parallel is with respect to the polarization of the source. This ratio is interesting because it can be different for different vibrations, so it is used to assign peaks. Asymmetric vibrations can have depolarization ratios as high as 6/7, while symmetric vibrations have much less depolarization.⁵

Resonance Raman refers to the collection of Raman spectra using a source energy near that of the electronic transition energy of the molecule. Instead of going to a virtual state as shown in Figure 1, the molecule is in an excited electronic state before releasing the light. This is similar to fluorescence, except that the molecule does not relax to the

ground vibrational state of the excited electronic state; it doesn't have time to relax, as Raman occurs on a time scale of less than 10^{-14} seconds.⁵ Going to an actual state instead of a virtual state makes the absorption of light by the molecule much more probable, so more radiation is scattered. Since this effect only occurs for those transitions which are close to the energy of the source, only a few bands at a time will be seen, which can be an advantage in many situations.

Surface-Enhanced Raman spectroscopy (SERS) is the practice of adsorbing the sample to a rough metal surface, sometimes a surface of silver nanoparticles, in order to get a signal enhancement of 10^5 or more. The enhancement could even be higher than 10^{10} in specific "hot spots".^{3f} SERS has been explained by the "em mechanism", which says that the metal nanoparticles cause an increase in the electromagnetic field near their surface, such that the energy absorbed and emitted by particles near the surface is greatly enhanced.^{3f} However, this mechanism does not explain the "hot spots" observed, and explaining SERS correctly is still a topic of current research.^{3f} One disadvantage of SERS is that adsorbing the sample to metal may cause its shifts to be different than they would be in solution, because its environment has changed.

Carbon nanotubes have been observed to have three major types of Raman bands. The lowest frequency Raman peaks, around $160\text{-}200\text{ cm}^{-1}$, are due to "radial breathing", the movement of the carbon atoms radially which causes the nanotube diameter to expand and contract.² These are sometimes called the R band and depend on the tube's diameter, meaning that observing these peaks could be a way of measuring tube diameter.² The other intense peaks of nanotubes occur around $1500\text{-}1600\text{ cm}^{-1}$, and are sometimes called tangential modes, or the T band. This can also be called the G band, as

it is similar to a band found in graphite. It is due to motion of the carbon atoms tangential to the surface of the nanotube. Two peaks are often observed in the T band because the atoms can move either parallel or perpendicular to the axis of the tube.² The third major feature of Raman spectra of nanotubes is the D band, which occurs around 1350 cm^{-1} and is due to defects in the nanotubes.

The D band has an overtone called the G' band (or D* band), which occurs around twice the frequency of that of the D band.^{3b} In a simplistic way, an overtone can be thought of as exciting the material to the second or higher vibrational level instead of the first vibrational level, so it occurs approximately at a multiple of the energy of the first transition (if the levels are evenly spaced). Combination modes which are not all fully understood also occur. Various methods, including single-nanotube Raman spectroscopy^{3g}, have been used to assign specific (n,m) values to their features in Raman spectra.

The D band is not independent of the excitation wavelength as it would be in the idealistic picture presented in the introduction. Variations in the D band amplitude can be understood with perturbation theory, and calculations involving this are shown in Kürti's paper.^{3c}

SERS has been used successfully for nanotubes, but the interaction between the nanotubes and the metal surface can be problematic.^{3d} SERS was used to study the "bundle effect", the shift in the radial breathing mode of the nanotubes depending on the number of tubes that are bundled together.^{3d} (Nanotubes can be found alone or in "bundles" in which they are aligned and hexagonally packed.) Specifically, Lefrant and

coworkers (reference 3d) found that the radial breathing mode peak was at 177 cm^{-1} for individual nanotubes and 194 cm^{-1} for bundles.

Other studies involving the change in Raman spectra with change in their immediate surroundings have included experiments on nanotubes with silver inside of them^{3a} and nanotubes in a polymer matrix⁶. Spectra of the nanotubes filled with silver had a broader T band and new features not seen in unfilled nanotubes, and the silver filling affected metallic nanotubes the most, causing a new peak at 1530 cm^{-1} .^{3a} Heating and then cooling the silver filled nanotubes caused their peaks to have much higher intensity, possibly because the heat annealed the silver filled nanotubes, eliminating some of the defects.^{3a}

There are many other applications of Raman spectroscopy to the study of nanotubes. Maultzsch and others^{3e} studied polarization dependent effects of carbon nanotubes. They were able to corroborate some of the existing theory about nanotube vibrations and found that the highest signal was observed when the source and emitted light were polarized parallel to the axis of the nanotubes.^{3e} Nanotubes subjected to a voltage were studied by Sood and Ghosh.^{3h} They found that applying a voltage across the nanotubes during resonance Raman measurements changed the intensity of the radial breathing mode, but did not affect the T band.^{3h} Research on the effects of pressure on the Raman spectra of nanotubes was recently reviewed.² Both the R and the T bands are affected greatly by pressure.²

Since many of the effects which can be measured by Raman spectroscopy were only discovered in the past few years, most of their possible applications have not yet been realized. However, Raman has been used to learn more about the carbon nanotube

systems and has been able to guide theorists in their description of nanotubes. With a better understanding of nanotubes, it is easier for researchers to get the nanotubes to perform as desired. With the help of Raman spectroscopy, carbon nanotubes will be put to use in more and more exciting new ways.

Summary of "Structure-Assigned Optical Spectra of Single-Walled Carbon Nanotubes"¹

This research involved combining resonance Raman spectroscopy with fluorescence measurements in order to assign peaks to single-walled carbon nanotubes (SWNTs) based on their specific (n,m) vector. The fluorescence measured was due to the band-gap in semiconducting SWNTs in suspension with a surfactant. Since the fluorescence was only seen in semiconducting SWNTs, those with an integer value of $(n-m)/3$ were not studied (these nanotubes are metallic or semi-metallic). 33 different (n,m) nanotubes were studied.

The peaks of the fluorescence were assigned to specific tubes by using the knowledge that the radial breathing mode (RBM) of nanotubes is related to their diameter and that the signal is enhanced by using excitation frequencies similar to the absorption frequencies (resonance Raman spectroscopy). By finding out which frequencies of excitation caused which RBM frequencies, it could be determined the diameters of the nanotubes with known fluorescence frequencies. Because the (n,m) value determines how big the rolled-up graphite sheet is, it determines the diameter, so the (n,m) values which correspond to fluorescence frequencies could be found.

This makes it possible for researchers to measure the fluorescence of a sample of nanotubes and determine which types of nanotubes are present and in what quantities.

One important application of this work is for people trying to separate different types of nanotubes. When trying a new method of separation, this research could provide a fast way to tell how well the different types of nanotubes are separated with the new method.

Summary of "Using Carbon Nanotubes to Detect Polymer Transitions"⁶

In this paper, single-walled carbon nanotubes (SWNTs) were mixed into polymers, and Raman spectra of the nanotubes were measured. The nanotubes' spectra changed based on the strain in the polymer, thus making the nanotubes like "nanoscale dimensional strain gauges". Because the properties of the polymer changed significantly at the glass transition temperature, the Raman spectra of the nanotubes were able to show when the polymer underwent various transitions. Dynamic mechanical thermal analysis of the polymers was also performed.

Two polymers were used: polyurethane acrylate (PUA) and amorphous bisphenol A polycarbonate (PC). About 0.1 weight percent of nanotubes were incorporated into each polymer. The PC, which is thermoplastic, could be dissolved in solution with the nanotubes. The solution was evaporated, leaving the desired material. However, the PUA was not dissolved because this could affect the curing process. So before curing the PUA, the nanotubes were incorporated into it by mixing with ultrasound vibrations.

Raman spectra of these materials were then taken at various temperatures from -180 °C to past the glass transition temperature (T_g) of the polymers. The main feature that was studied was the D^* band peak wavenumber. For the PC, the D^* band moved from 2630 cm^{-1} at 25 °C to 2642 cm^{-1} at -160 °C . The same trend was observed for PUA. The paper lists three reasons (all occurring together) for a shift in wavenumber. First,

SWNTs normally have a shift like this, even when not in a polymer, but it is much smaller. Second, the cohesive energy density causes depends on temperature, causing changes in stress with changing temperature, and therefore causing changes in the Raman spectra. Finally, there is thermal residual strain resulting from the cooling of the polymer, which changes the stress on the nanotubes.

However, these three processes do not explain the peaks which were observed in the wavenumber versus temperature plots. These peaks correspond to well-known transitions in the polymers, which signify different types of relaxation of the polymer molecules. The temperatures of these transitions can be read from the wavenumber versus temperature graph, so the nanotubes proved to be an effective probe into polymer transitions.

Sketch of a Proposal

Polymer nanocomposites have been the subject of much recent research because of the enormous potential to tune their mechanical, optical, thermal, or electrical properties by simply changing the nanoparticle size, volume fraction, polymer-particle interfacial attraction, or other experimentally controllable parameters. However, most of the theoretical and computer simulation work so far has been done on composites of polymers and approximately spherical fillers such as silica. I am interested in carbon nanotubes as fillers. Anisotropic fillers such as nanotubes can potentially align in the polymer matrix, and their effect on the organization of nearby chain molecules could cause the composite to exhibit qualitative differences from its spherical particle analog.

This is why further experimental and theoretical work is needed to understand these systems and take full advantage of their interesting properties.

I find these systems interesting because nanotubes have a high strength to weight ratio, but they slide past each other if made into a small rope. Therefore, putting them in a polymer matrix may be the only way to harness their strength. Also, because nanotubes have such interesting electrical properties, their composites have many potential applications, especially if they can be aligned. It is remarkable that fillers in very small quantities can noticeably change the polymer's properties. For instance, each nanotube might be strongly attracted to the surrounding polymer, causing the polymers nearby to arrange themselves to make as much contact with the nanotube as possible. This new induced order may then affect the polymers throughout the nanocomposite.

Zhao and coworkers used nanotubes in a polymer matrix as "spies" which could show them how the polymer itself was acting.⁶ They weren't interested in the interaction between the nanotube and polymer as much as what the nanotube could tell them about the polymer itself. I think the same sort of measurements could be applied to understand the interaction between polymer and nanotube. The nanotubes were shown to be like tiny strain gages⁶, so when strain is applied at different frequencies, the transfer of that strain to the nanotubes can be measured. The Raman spectra could be done at different temperatures, pressures, and strain frequencies in order to understand how the nanotubes work with the polymer. Also, it could be done for nanotubes which are functionalized--they have chemical groups attached to them. Functionalizing nanotubes in different ways would allow control of the interfacial attraction between the nanotube and polymer. The

effect of the attraction on the nanotube-polymer system could then also be measured with Raman spectroscopy.

This type of study could guide theoreticians to better explain the polymer-nanotube composites. Relatively simple models and theories, simply not currently available for these systems, would provide insight into the main causes of observed behavior and suggest strategies to optimize various properties. This would hopefully lead to more directed, efficient experiments and new directions for future research.

References

- ¹Bachilo, Sergi M. et al. "Structure-Assigned Optical Spectra of Single-Walled Carbon Nanotubes", Science 2002, Vol. 298, p 2361-66.
- ²Loa, I. "Raman Spectroscopy on Carbon Nanotubes at High Pressure", J. Raman Spectrosc. 2003, Vol. 34, p. 611-21.
- ³Proceedings of the Eighteenth International Conference on Raman Spectroscopy, Ed. János Mink, György Jalovsky, and Gábor Keresztury; West Sussex, England: Wiley and Sons, 2002.
- ^aCorio, P. et al. "Characterization of Single Wall Carbon Nanotubes Filled with Silver Chloride" p 455-56.
- ^bFilho, A. G. Souza et al. "Dispersive Raman Modes in Isolated Single Wall Carbon Nanotube" p. 481-82.
- ^cKurti, J. et al. "'Triple Resonant' Raman Scattering in Single Wall Carbon Nanotubes: Oscillations in the D and D* Bands" p. 49-52.
- ^dLefrant, S. et al. "Raman and SERS Studies of Carbon Nanotubes Systems" p. 473-74.
- ^eMaultzsch, J. et al. "Polarized Raman Measurements in Zeolite-Grown Single-Wall Carbon Nanotubes" p. 475-76.
- ^fMoskovits, Martin. "Surface-Enhanced Raman Spectroscopy--Past and Future" p. 53-54.
- ^gSaito, R. et al. "Theory of Raman Scattering in Single Wall Carbon Nanotubes" p. 441-42.
- ^hSood, A. K. and Shankar Ghosh, "Single-Wall Carbon Nanotubes: Electrochemical Effects" p. 445-46.
- ⁴Robinson, L. C. Methods of Experimental Physics, Volume 10: Physical Principles of Far-Infrared Radiation, New York: Academic Press, 1973.
- ⁵Skoog, Douglass A., F. James Holler, and Timothy A. Nieman. Principles of Instrumental Analysis, 5th ed. Philadelphia: Harcourt, 1998.
- ⁶Zhao, Qing, Jonathan R. Wood, and H. Daniel Wagner. "Using Carbon Nanotubes to Detect Polymer Transitions", J. Poly. Sci. Part B: Poly. Phys. 2001, Vol. 39, p 1492-95.