Low-Frequency Raman Spectra of Carbon Nanotubes Measured with an Astigmatism-Free Schmidt-Czerny-Turner Spectrograph

Abstract

Traditional Czerny-Turner (CT) spectrographs suffer from the optical aberration called astigmatism. This causes Raman peaks measured with CT spectrographs to be broadened and short, decreasing spectral resolution and signal-to-noise ratio (SNR). The new IsoPlane ISOPLANE 320 Schmidt-Czerny-Turner ("IsoPlane") spectrograph from Princeton Instruments has zero astigmatism at all wavelengths across the entire focal plane. This means Raman spectra measured with an IsoPlane have better resolution and SNR compared to spectra measured with a traditional CT spectrograph.

An IsoPlane has been interfaced to a low frequency Raman module that enables measurement of peaks with Raman shifts as low as 10 cm^{-1} using only a single stage spectrograph. Calculations show that the unique ability of this system to detect low frequency Raman peaks should allow the study of nanotubes much larger in diameter than is currently possible.

Introduction

The Czerny-Turner (CT) spectrograph has been used to measure Raman spectra of samples for decades[1, 2]. Inherent in the design of the CT spectrograph are optical aberrations including astigmatism[3]. Astigmatism occurs when mirrors are used to focus a source off axis, giving a ray that is elongated in the horizontal and vertical directions. Astigmatism is particularly large at the edges of the focal plane, and is present in CT spectrographs regardless of their manufacturer. The impact of astigmatism on images is to make them blurry, poorly resolved, and dim.

Fluence is a measure of the number of photons hitting a unit area of a detector and is given by

$$F = N/A \qquad (1)$$

*Where*
F = Fluence
N = # of photons
A = Area

Because astigmatism causes light rays to spread out in the horizontal and vertical directions fewer photons fall on a greater area of the detector, decreasing fluence. The effect on spectral peaks is to make them broadened and short, giving peaks with poor spectral resolution and SNR (in this context SNR is defined as peak height divided by the noise measured in the baseline immediately adjacent to a peak).

The advantages of the Princeton Instrument's IsoPlane spectrograph for measuring Raman spectra are seen in Figure 1.

Figure 1.

Spectra of the 802 cm-1 cyclohexane Raman shift peak. Note the spectrum measured with the IsoPlane Schmidt-Czerny-Turner (ISOPLANE) spectrograph is narrower and taller than the same peak measured with a Czerny-Turner (CT) spectrograph.
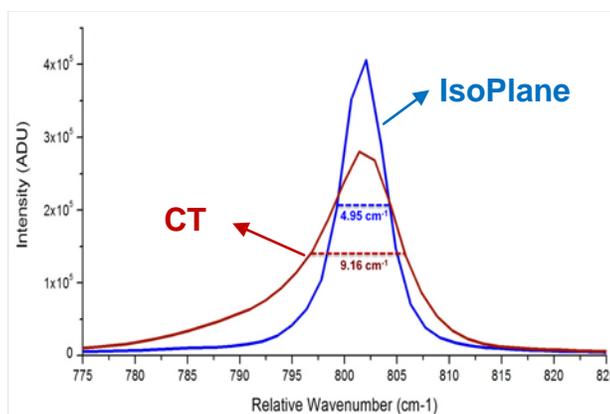
The figure shows the 802 cm-1 Raman shift peak of cyclohexane measured with a CT and IsoPlane spectrographs. Note the CT peak is broad and short. Princeton Instruments has developed the IsoPlane SCT 320 Schmidt-Czerny-Turner spectrograph ("IsoPlane"). The IsoPlane has zero astigmatism at all wavelengths across the entire focal plane. The cyclohexane Raman peak measured with an IsoPlane seen in Figure 1 is narrower and taller than the equivalent peak measured with a CT spectrograph. This shows that the IsoPlane can measure Raman spectra with better spectral resolution and SNR compared to the CT spectrograph

Low frequency (10-200 cm-1) Raman bands provide information on lattice modes in solids, and can be used to distinguish active pharmaceutical ingredient polymorphs from each other[4, 5]. A new low frequency Raman analysis system from Ondax Inc.[6] uses volume holographic gratings to filter the Rayleigh line. As shown in Figure 2, this system allow bands 10 cm^{-1} away from the Rayleigh line to be observed using only a single stage spectrograph. The Ondax Raman front end has been interfaced with an IsoPlane to give a system that is small, easy to use, and provides astigmatism free low frequency Raman spectra.

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It is well known that the low frequency Raman shift of carbon nanotubes due to their radial breathing mode is inversely proportional to diameter[7]. The IsoPlane-based low frequency Raman system described herein has been used to obtain spectra of a collection of carbon nanotubes. The ability of this system to see peaks with Raman shifts as low as 10 cm^{-1} will allow researchers to determine the diameter and properties of carbon nanotubes much greater in diameter than previously possible.

Experimental

L-cystine and single wall carbon nanotubes were purchased from Sigma-Aldrich (St. Louis MO) and analyzed as is in glass vials. The vials had a reproducible but small fluorescence spectrum that was subtracted from sample spectra prior to data workup.

The XLF-CLM Raman analysis system from Ondax (Monrovia CA) was used to generate low frequency Raman spectra. This module contains a sample holder, focusing objective, 785 nm SureLock^{TM} laser, amplified spontaneous emission filters, a neutral density filter, and SureBlock^{TM} proprietary, solid-glass, volume holographic gratings with an optical density >8. Light was collected in a 180° backscattering mode. A laser power of 50 milliwatts was used. Light from the Ondax system was coupled to the spectrograph via a single core 25 micron diameter optical fiber with NA = 0.1.

The XLF-CLM was coupled to a Princeton Instruments (Acton MA) ISOPLANE 320 ("IsoPlane") Schmidt-Czerny-Turner spectrograph. This spectrograph has a focal length of 320 mm and was equipped with a 600 groove/mm grating blazed at 500 nm. The wavelength axis of the spectrograph was calibrated using a series of Hg arc lamp lines and the Princeton Instruments (Trenton NJ) IntelliCal^{TM} wavelength calibration system. The accuracy of the wavelength calibration reported by the software was 0.01 nm. The calibration was checked by measuring the low frequency Raman spectrum of sulfur and comparing it to the literature[7]. The measured and literature peak positions for eight sulfur peaks between 20 and 220 cm^{-1} agreed with a standard deviation of 0.57 cm^{-1}. All Stokes peak positions listed below had corresponding anti-Stokes peaks.

The camera used was a Princeton Instruments (Trenton NJ) Pixis 400BRX back illuminated deep depletion sensor that was treated with the Excelon® process. The CCD was cooled to -70° C. A region of interest 15 rows tall was defined and all rows in this region were vertically binned. Sensor rows outside of this region were found to contain negligible counts. The equipment was controlled and data collected using Princeton Instruments (Trenton NJ) LightField software V4.5. Data were processed and displayed using GRAMS V9.1 software from ThermoFisher Scientific (Waltham MA).

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Results and Discussion

L-cystine is known to have a peak with a Raman shift of 10 cm-1 [6, 8]. The Raman spectrum of L-cystine measured with the IsoPlane based system described above is shown in Figure 3.

There are clearly Stokes and anti-Stokes peaks at 9.7 cm^{-1}, indicating that this system is capable of measuring Raman shifts as low as 10 cm^{-1}.

The low frequency Raman spectrum of a collection of carbon nanotubes is seen in Figure 4.

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Figure 3. *Low frequency Raman shift spectrum of the amino acid L-cystine showing Stokes and anti-Stokes peaks near 10 cm^{-1}.*
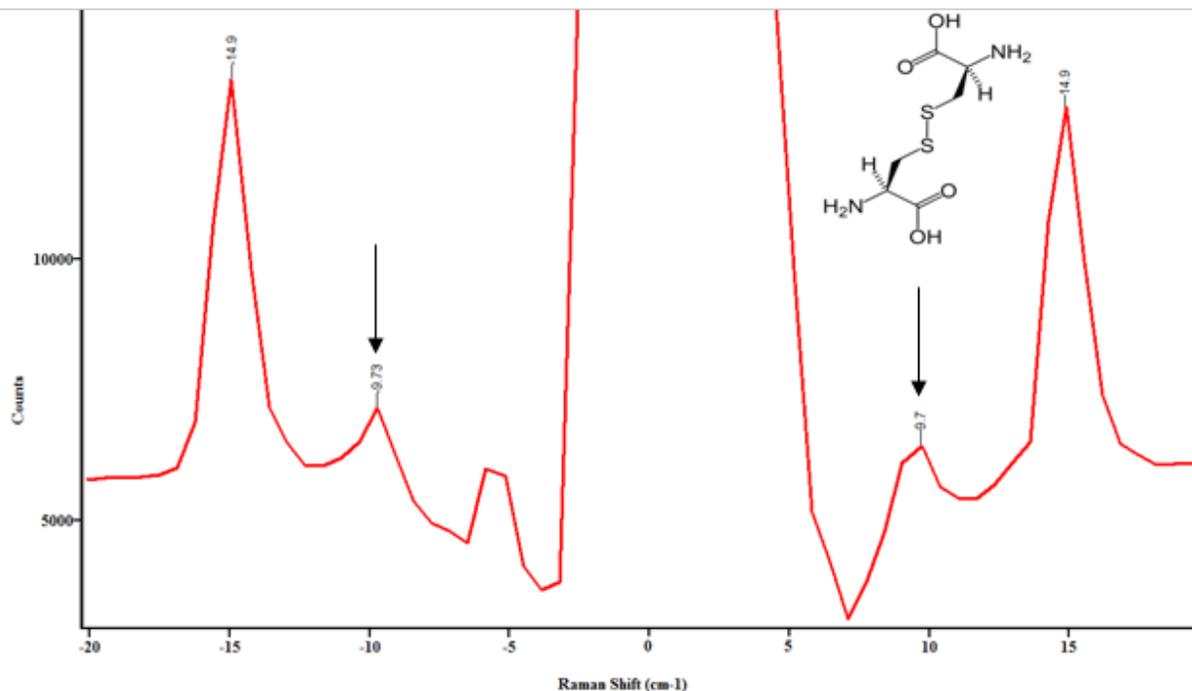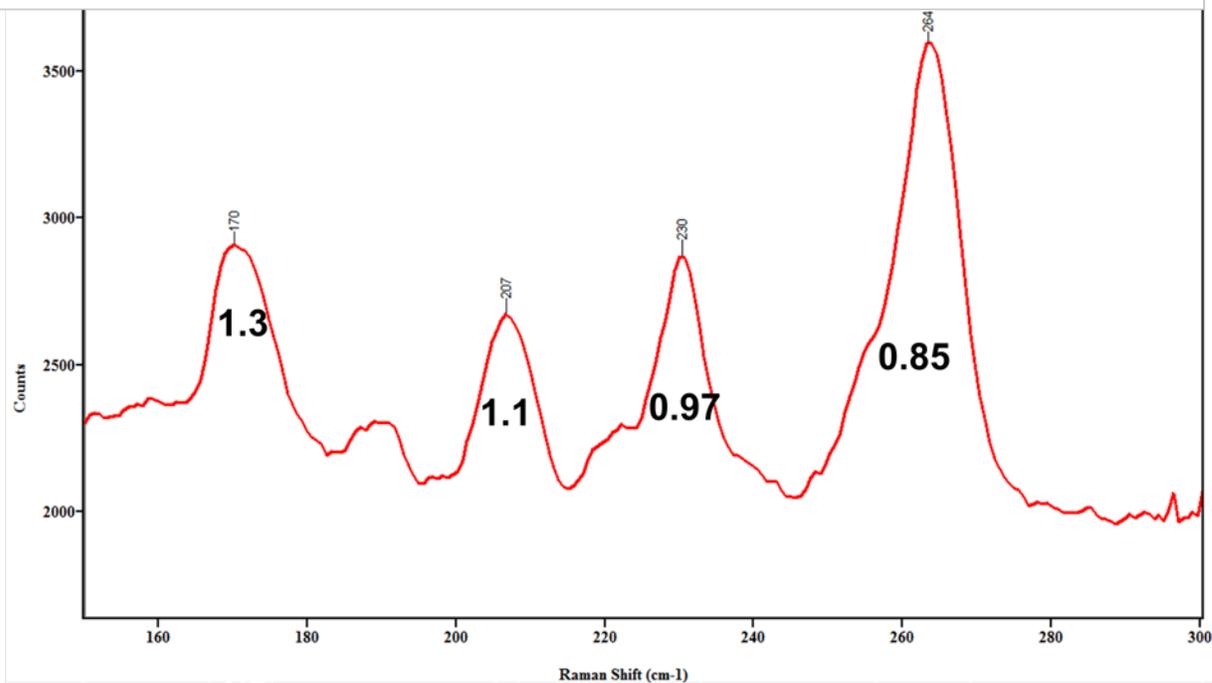

Figure 4. *The Low-frequency Raman spectrum of a collection of single wall carbon nanotubes 0.7 to 1.3 nm in diameter. The peak positions of these ring-breathing modes correlates to tube diameter. The tube diameters in nm calculated from this spectrum are marked under each peak.*

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The four peaks are radial breathing modes (RBM). The diameter of a nanotube can be determined from the RBM peak position using the following equation [7]

$$D_t = 224/W \qquad (2)$$

Where
D_t = Tube diameter in nanometers
W = Wavenumber of the radial breathing mode peak

Using this equation and the peak positions in Figure 3, diameters of 1.3, 1.1, 0.97, and 0.85 nm for the tubes contained in the sample were determined. These diameters are listed under the corresponding RBM peak in Figure 4. The results show this sample contains at least four populations of nanotubes with different diameters. These results are consistent with the manufacturer's statement on the bottle that the tubes are from 0.7 to 1.3 nm in diameter.

Low frequency Raman spectra are difficult to measure because of the proximity of these peaks to the Rayleigh line. Thus many Raman systems can only see peaks with Raman shifts as low as 100 cm^{-1}. Using equation 2, this means that only carbon nanotubes 2.24 nm in diameter and smaller can be studied.

We have shown above that the current system can see peaks with Raman shifts as low as 10 cm^{-1}. Combining this fact with equation 2 means carbon nanotubes with diameters as large as 22.4 nm can now be characterized and studied using the system described herein, extending the field of research for these very important materials.

A disadvantage of the current system is that the volume phase holographic gratings used to filter the laser line only work at a fixed excitation wavelength, in this case 785 nm. Researchers who desire to use several excitation wavelengths will have to purchase multiple low frequency Raman front ends at a cost of tens of thousands of dollars per system. Workers who wish to perform low frequency Raman spectroscopy with multiple excitation wavelengths should consider using a triple monochromator system such as the Princeton Instruments TriVista.

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CONCLUSIONS

1. The Princeton Instrument's IsoPlane spectrograph gives improved Raman spectra compared to Czerny-Turner spectrographs.

2. An IsoPlane combined with an Ondax low frequency Raman front end makes measuring quality carbon nanotube spectra fast and easy

3. The system sees peaks as low as 10 cm-1, greatly increasing the diameter of single wall carbon nanotubes that can be analyzed.

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For more information about IsoPlane visit: www.princetoninstruments.com

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