

Developing the Optical Instrumentation for Micro-Raman Spectroscopy (DOIMS)

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Abstract—This paper demonstrates the development of a micro-Raman setup for analyzing the chemical nature of different samples by microscopic examination. As in every Raman setup, the sample is irradiated by a laser beam. The backscattered radiation from the sample is collected by a microprobe and fed to a spectrograph that images the Raman spectrum on to a highly sensitive detector. The detector data is then displayed and analyzed with the help of suitable software. By interpreting the Raman spectrum, an unknown material can be identified and also the material can be fully characterized. Here a fully functional Micro-Raman spectrometer was developed and the system was evaluated by analyzing Raman standard samples like diamond, CCl_4 and paracetamol.

Index Terms—iHR320,Raman Spectroscopy, Spectrograph, Synapse CCD, Ultra Big Sky Nd YAG laser

1) INTRODUCTION

Raman spectroscopy is an important technique for determining the structure and chemical composition of a solid, liquid, or gas by mapping its vibrational spectra. The main principle behind Raman spectroscopy is Raman scattering. It is the change in the wavelength of the incident light when it is deflected by molecules of a sample. When a light beam is focused on to a chemical sample, most of the scattered light is of same wavelength as that of incident wavelength. A small portion has wavelengths different from that of the incident light which is due to Raman Effect. In other words, when the incident light strikes the molecules of a sample, most of the encounters are elastic (the photons are scattered with unchanged energy and frequency). In some cases, the molecule in the sample absorbs energy from or gives the energy to the photons and the photons scatter with diminished or increased energy (hence with lower or higher frequency). This frequency shift gives the amount of transition between the initial and final states of the scattering molecule. Thus we get the Raman pattern which is the characteristic of the particular molecular species and its intensity is proportional to the number of scattering molecules in the path of the light. Thus Raman spectra can be used for qualitative and quantitative analysis.

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In Raman spectroscopy, the sample is irradiated by intense laser beams in UV-Visible region (ν_0) and the scattered light is observed in the direction perpendicular to the incident beam. The scattered light has two components: the major part called the Rayleigh component is strong and has the same incident frequency (ν_0). The weaker part called Raman component has frequency $\nu_0 \pm \nu_m$ where ν_m is the vibrational frequency of the molecule. $\nu_0 - \nu_m$ and $\nu_0 + \nu_m$ are called Stokes and Anti-Stokes lines respectively. Thus the vibrational frequency (ν_m) is measured as a shift from the incident frequency (ν_0). Stokes and Anti-Stokes scattering are weak compared to Rayleigh. Still they provide the most important compositional and structural information on the molecules present in the sample.

2) INSTRUMENTATION

Generally there are four major sections for the Raman spectroscopy systems. The schematic diagram of the micro-Raman spectroscopy system is shown in Figure 1 and described in detail below.

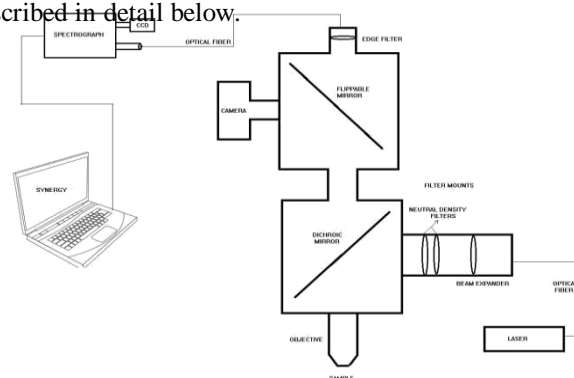


Fig.1: Schematic diagram of the Micro-Raman spectroscopy system.

A. Excitation Source

This is generally a monochromatic light of known wavelength that is directed towards the sample and scattered by the molecules in the sample. The excitation source used for this study is a mini Nd: YAG pulsed laser from Quantel Big Sky Laser (model Ultra) with a 532 nm wavelength, 30 mJ/pulse total energy, up

to 20Hzlasing frequency, and 8 ns pulse width. The laser beam is made to focus on the sample using a dichroic mirror. The 180° back scattering configuration used here permits maximum scattered signal to be collected from the target. Thus maximum performance is achieved.

B. Light Collection System (Microprobe)

The scattered photons from the sample are collected using a microprobe. The microprobe should be designed in such a way that it should collect maximum amount of scattered light and at the same time block the strong Rayleigh scattered signal. Here the collection optics consists of the following parts:

- Dichroic Filter Mount: A 30mm cage system that can hold filters and mirrors.
- Dichroic Mirror: Reflects light over a certain range of wavelengths and transmits light which is outside that range.
- Objective: Generally a 20X objective is used for collecting the backscattered light from the sample.
- Raman Edge Filter: Blocks the laser wavelength, strongly attenuates the Rayleigh signal and transmits all other wavelengths.

C. Spectrograph

The collected light is then passed through a spectrograph, via optical fiber coupling. The Spectrograph used here is a fully automated imaging spectrometer iHR 320. The transmitted signal is focused on to a 100 μm slit that defines the resolution of the spectral lines. This is then passed through a holographic transmission grating which will disperse the signal into its spectral components. The transmission grating disperses two spectral tracks on the detector. The low frequency portion is dispersed on the upper half of the detector, while the high frequency portion is dispersed on the lower half. This feature makes the range of the spectrograph double thereby maintaining the spectral resolution.

D. Detector

The output from the spectrograph is then detected using an array of photodetectors. The detector used here is a thermoelectrically cooled, gated, and intensified charge coupled device (ICCD) (Synapse ICCD) with 1024 x 256 pixels, and 26 μm x 26 μm pixel size. In the ICCD, the input light signal is first passed through a photocathode thereby releasing electrons from the incident photons. This increases the gain up to 250 to the input signal for detecting the extremely weak Stokes lines.

The released electrons are then passed through microchannel plates (MCP). More electrons are generated as they hit the channel walls. These electrons then strike the phosphor coating on a fluorescent screen releasing photons which then fall on the CCD pixels thereby generating charge. The horizontal position of the charge will be the horizontal position of the spectral line and the amount of charge generated defines the intensity

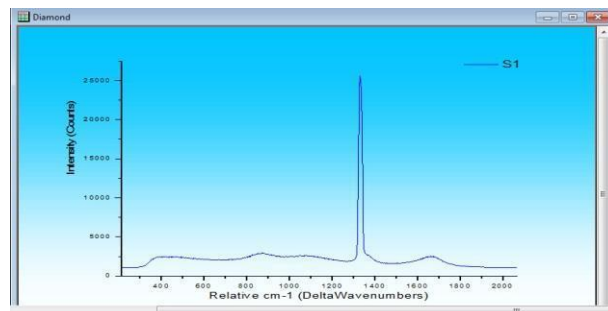
To display and analyze the resulting spectra, the CCD is connected to a computer, which contains the CCD application software. Here, the spectra are processed and analyzed using SynerJY 3.5 software.

3) EXPERIMENTAL PROCEDURE

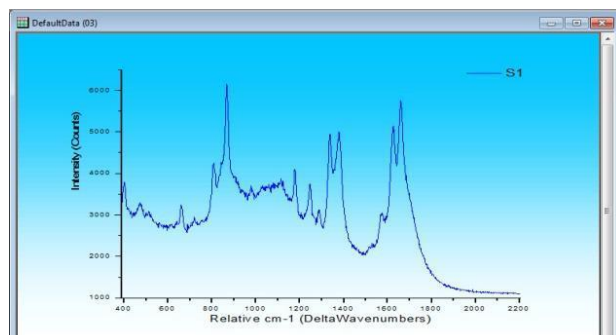
Samples are placed below the objective. To collect the Raman spectrum for each sample, the laser is fired, and the CCD is turned on for an integration time of 10 seconds. Now the Raman spectra can be recorded.

4) RESULTS AND DISCUSSION

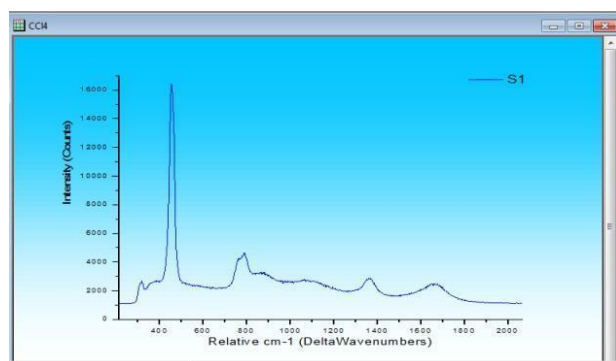
To evaluate the system, the Raman spectra of Diamond, CCl₄ and Paracetamol were measured. The integration period of 10s was enough to generate high quality Raman spectra with highly defined peaks and bands. The spectra obtained for different samples are shown in Fig2.



(a)



(b)



(c)

Fig.2: Raman spectra obtained for (a) diamond, (b) paracetamol and (c) CCl₄

For diamond, the characteristic fingerprint is a single sharp peak at 1332cm^{-1} . Thus Raman spectroscopy can be used for non-destructive characterization of diamond and diamond-like materials.

For Paracetamol, the characteristic bands are at 1650cm^{-1} , 1612cm^{-1} , 1329cm^{-1} and 799cm^{-1} . This can be used for mapping the distribution of chemical compounds in the tablet.

For CCl_4 , the strongest line occurs at 459cm^{-1} . This can be used for monitoring polluting chemicals in the environment.

5) CONCLUSION

A Micro-Raman spectroscopy system was demonstrated, having the ability to measure the spectra of different samples in light on condition. The Raman spectra of standard samples, diamond, CCl_4 and paracetamol verified the performance of the system.

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