

A low cost laser-Raman spectrometer

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Abstract. A Jobin Yvon-Spex (HR640) monochromator with a notch filter (514.5 nm) and Ar⁺ ion laser has been used to set up a low cost laser Raman spectrometer. The selection and setup of the various optical components used in the present work has been solely carried out in our laboratory. The calibration of the monochromator was established from the studies of various standard mercury lines and the obtained data fitted with the reported data. Raman signals have been recorded for a number of samples e.g. diamond, ruby, carbon tetrachloride (CCl₄), benzene (C₆H₆) and ethanol (C₂H₅OH). The obtained results are found to be in excellent agreement with the reported values for these materials in the literature.

Keywords. Raman spectrometer; laser Raman spectroscopy.

1. Introduction

Since its discovery in 1928, Raman spectroscopy has proved to be an invaluable, powerful and widely used optical method for investigating the dynamics of different states of matter. In the early years, experiments were carried out using mercury sources, prism spectrographs and photographic detection techniques (Bansal *et al* 1976). However, the techniques and instrumentation in Raman spectroscopy have undergone considerable changes during the last few decades. The availability of lasers as intense, monochromatic and polarized excitation sources enables one to record weak scattering spectra and its applications are attached widely over the fields of physics, chemistry and bio-science (Tonino and Okushi 1990). Conventional laser-Raman spectrometer employs a monochromator for spectral dispersion and photo-multiplier for detection of light signal (Gardiner and Graves 1989; Roy *et al* 1992), which corresponds to a single channel detection system. However, several improvements have been incorporated for ease in handling and operation of the instrument. Typical setups consist of (i) a CW laser which emits monoenergetic beam, (ii) steering or source sampling optics which directs the beam towards the sample, (iii) a single stage monochromator with computer controlled scanning for spectrally analyzing the inelastically scattered radiation from the sample and (iv) PMT or CCD for detecting Raman signal with associated photon counting system linked to computer for data acquisition and analysis. This type of setup allows for a fast acquisition of Raman spectra over a large spectral range but its inherent

limitation is the rather low resolving power (Roy and Bansal 1988; Panitz *et al* 1994).

With fast advancement in technology, multiple grating monochromators with charged coupled device (CCD) arrangement or multichannel signal acquisition spectrometers are being used. Although these instruments provide higher resolving powers, however, their use is limited by their expensive components. The throughput of double or triple monochromators is smaller in comparison to the single monochromators. Moreover, in high resolution experiments, the intensity is spread over a large number of channels (Engert *et al* 1994). CCDs provide increase in quantum efficiency and very low dark count rates resulting in increase in sensitivity (Carter and Pemberton 1995). However, the use of multichannel detection system also suffers from some inherent disadvantages as compared to single channel detection system such as small dynamic range of the array detector and restricted density of measurement points depending upon the dimensions of single detector element. In addition, the spectral range is limited by both the overall dimension of the detector and the dispersion of the monochromator (Deckert and Kiefer 1992; Engert *et al* 1994).

In this context we have used a low cost single stage monochromator with single channel signal acquisition system whose optical steering system has been indigenously setup. The room temperature Raman spectra were recorded using 514.5 nm line of 4 W argon ion laser in backscattering geometry. The Rayleigh line was filtered from the exciting line by a notch filter. The laser light was steered through a long optical path with the help of a series of highly polished mirrors and lenses. The various components of this low cost laser-

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Raman spectrometer and their advantages are described in the following sections. The calibration as well as spectra of some of the materials studied are described in later sections of this paper.

2. The spectrometer

2.1 Laser source

An argon ion laser is an important and powerful excitation source for light scattering. It can provide several discrete lines. The most important of these lines are centred at 488 nm and 514.5 nm (Roy and Bansal 1988). A Coherent Innova 70 argon ion laser is used to conduct our experiments. It can be operated in the single-line or multiline mode with an all line power output of 4 W. We have used an excitation wavelength of 514.5 nm (green radiation) with a beam diameter of 1.5 mm and a beam divergence of 0.5 mrad. An SCR (Silicon-controlled rectifier) is used to provide DC current to the plasma tube, magnet and power supply electronics. The laser head cooling is done by a PolarPure 12 laser chiller.

2.2 Focussing optics

The optical components used for focussing the laser beam, are used in a configuration which helps to minimize the intensity loss from the incident as well as the scattered radiation from the sample. These components have been purchased from M/s Melles Griot, Holland. The selection of these optical components was based on a detailed estimation of several optical parameters, in particular, focal length of the combination of collecting lenses, the dispersivity of the prism, mirror reflectivity etc with a view to obtain maximum efficiency. As shown in the schematic diagram (figure 1), the output of the laser source is allowed to fall on a beam steerer which comprises of two vertically displaced, highly reflecting

plane mirrors (average reflectance $\sim 92\%$) placed at 90° to each other and at 45° to the vertical axis, which result in a vertical displacement of the beam to the level of the entry slit of the monochromator. The beam is now directed towards a right angled prism which has a surface flatness of $\sim 95\%$. This prism reflects the beam at an angle of 90° towards a small mirror (5 mm diameter). Another reflection at this mirror surface (at 45° to the incident beam) allows the beam to fall on the sample in a 180° or back scattering geometry. Due to small size of the mirror the Raman signal back scattered from the sample which is usually very weak (1 in 10^5), is not hindered. This scattered beam from the sample is imaged on to the entrance slit of the monochromator using a collecting and a focussing lens with focal lengths 150 mm and 200 mm, respectively. In case of liquid samples a spherical mirror is placed behind the sample so as to minimize losses of the scattered radiation from the sample.

2.3 The monochromator

A single stage Jobin Yvon-Spex HR 640 Czerny-Turner monochromator is used for our measurements. It has a focal length of 0.64 m. Its low degree of deviation confers high performance characteristics on the instrument in terms of ultimate resolution. In addition, a good throughput is achieved due to large useful size ($80 \times 110 \text{ mm}^2$) of the holographic grating which has 1200 grooves/mm blazed at 500 nm. The grating is moved by a stepper motor controlled by the software described below. The mechanical scanning range of the monochromator is from 0–1500 nm. Two identical input and output slits with straight blades are used. The dispersion of the instrument is 12 Å/mm at 500 nm and the resolution is 0.16 Å at 546 nm and 2 mm high, 5–10 μm wide slits. The programmable scanning speed is continuous from 0.02 to 3000 Å/mm. The stray light level is less than

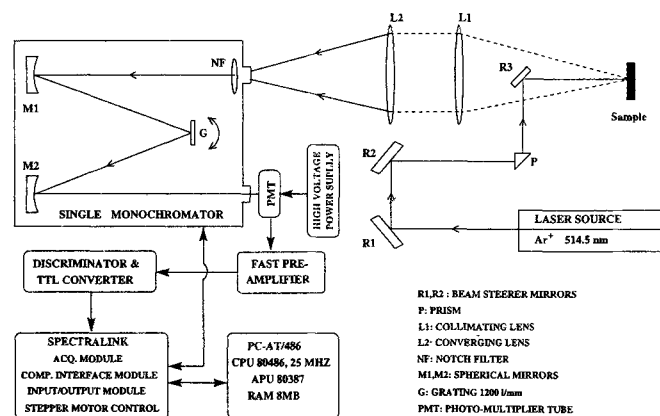


Figure 1. Schematic diagram of laser Raman spectrometer setup used for the present work.

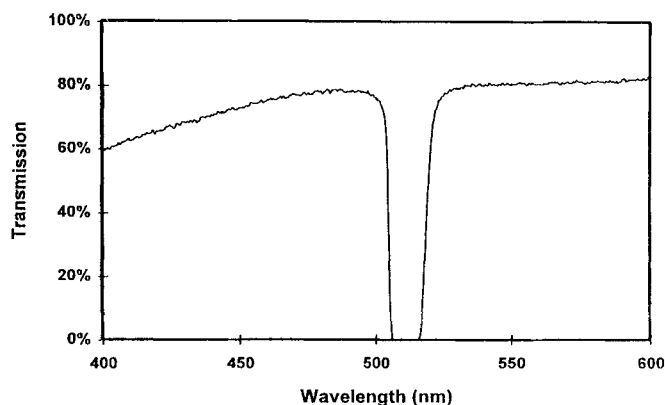


Figure 2. Transmission profile of the notch filter used for the present work.

10^{-5} at 10 Å with slits 20 μm wide and 2 mm high. The precision is ± 5 Å from 0 to 15000 Å with a repeatability of 0.2 Å.

A notch filter is used just before the entry slit of the monochromator to attenuate the Rayleigh line. It has an optical density of 4.3 and a spectral bandwidth of 575 wave numbers. Figure 2 shows the transmission characteristics of the filter used. The use of Rayleigh line rejection filters is essential since the stray light suppression of the single monochromator is often not sufficient for Raman spectroscopy, especially at low Raman shifts. Rayleigh filters represent an efficient and low cost alternative to the otherwise necessary filter stage in the expensive triple monochromator. It has been reported that efficient filters with high optical density at the laser frequency and sharp onset of absorption can replace the prefilter stage of the triple monochromator. The result is not only a large optical throughput but also a compact Raman instrument (Shulte 1992).

A photomultiplier tube (PMT) is used for the detection of the signal at the exit slit. The spectrally analyzed light emerging through the slit is detected using a R928 S PMT phototube in photon counting mode. The photon counter consists of HV supply, fast amplifier, discriminator and TTL converter controlled through the 'Spectralink' described later.

Thus the laser light scattered from the sample passes through the entry slit of the single monochromator which is placed in the focal plane of the spherical mirror M1 (figure 1) and is collimated to the grating G which disperses the signal. The diffracted beam is focussed by the mirror M2 onto the exit slit. Prior to falling onto the mirror M1, the light is made to pass through the notch filter described earlier. Low stray light levels are achieved due to this filtration despite using a single grating monochromator.

2.4 The spectralink

The monochromator control and data acquisition are executed by a modular system known as 'Spectralink'. It consists of many modular sub-units. There is a single high voltage power supply programmable from 0–2000 V (through the software) for the PMT. An acquisition module for monochannel detection with an integration time of 1 ms to 65 s is also provided. This module consists of a programmable photon counter and a dc amplifier. This module is used for acquisition of analog signals coming from the photo-multiplier tube. A computer interface module provides communication between the spectralink and the computer. In addition, spectralink also has an input-output module. A stepper motor control module is also a part of the spectralink. It is used for manually setting the monochromator position via a joystick, though it is programmable via the interface board

and the computer. This module is used to access built-in scanning functions (scanning speed, number of cycles and range of wavelength etc).

2.5 Software

2.5a Data acquisition: The data acquisition and parameter control is carried out through the 'Spectramax' software written in 'C' language provided by the Jobin-Yvon company. The spectramax software is a completely integrated series of programs and spectral routines for the acquisition and treatment of spectroscopic data. It has been written to work with MS DOS versions 5.0, 6.0 or higher. Spectramax utilizes the GEM graphical user environment as an operating environment for its windowing capability. The software allows for a flexible use of most standard modes of acquisition and helps in creation, storage and modification of acquisition routines.

2.5b Data analysis: The analysis of the experimental data obtained from the Raman measurements is carried out using the 'Peakfit' commercial non-linear curve fitting package. This package provides for data editing, conversion of units, deconvolution of the peaks, calculation of peak area as well as the line width. The observed Raman peaks in the present study have been fitted with a Voigt fit using Voigt function given by the equation:

$$f = \frac{\int_{-\infty}^{+\infty} \frac{a_0 \exp(-y^2)}{a_3^2 + \left[\left(\frac{x - a_1}{a_2} \right) - y \right]^2} dy}{\int_{-\infty}^{+\infty} \frac{\exp(-y^2)}{a_3^2 + y^2} dy},$$

where a_0 is the peak amplitude, a_1 the peak centre, and a_2 and a_3 determine the width of the peak (Dilawar 1997).

For a sharp peak and an isolated band the fitting procedure produces same peak characteristics with a decimal point accuracy. However, for broad bands, the uncertainty in position and width is within $\pm 5 \text{ cm}^{-1}$.

3. Calibration

The calibration of the instrument was carried out using a low pressure Hg light source. The entry and the exit slits of the monochromator were opened to a size of 50 μm each. The wavelength counter was set to zero to verify that maximum light flow leaves the instrument via the exit slit. The grating and the mirror position were adjusted in order to bring zero order into the exit slit. Thereafter the Hg spectrum was obtained in the wavelength range 500 nm–850 nm. A number of lines

were obtained which have been found to be in excellent agreement with the standard Hg lines (Jobin Yvon-Spex 1996) as shown in table 1. A plot of obtained wavelengths versus the standard wavelengths is shown in figure 3 which shows a linear correlation between the two.

4. Sample study

Subsequent to the installation and set up of the instrument as detailed in the above sections, a number of samples were studied which include solid as well as liquid samples. The results obtained for a few representative samples are discussed in the following sub-sections.

4.1 Diamond

Diamond is one of the few materials which has revolutionized many a technology e.g. high pressure physics, thin films, electronics etc. We have studied a type IIa natural diamond with 0.5 watt laser power at the source. The spectrum so obtained is shown in figure 4. It is clear from the figure that a very sharp Raman transition is obtained which is found to be centred at 1333.1 cm^{-1} .

Table 1. Comparison between the standard Hg Raman lines and the experimentally obtained lines.

Sl. No.	Expt. observed Hg lines (position in nm)	Std. Hg lines (position in nm)
1	545.4	546.00
2	576.8	576.90
3	580.2	579.70
4	626.2	626.30
5	668.2	668.30
6	729.4	730.02
7	809.4	809.30

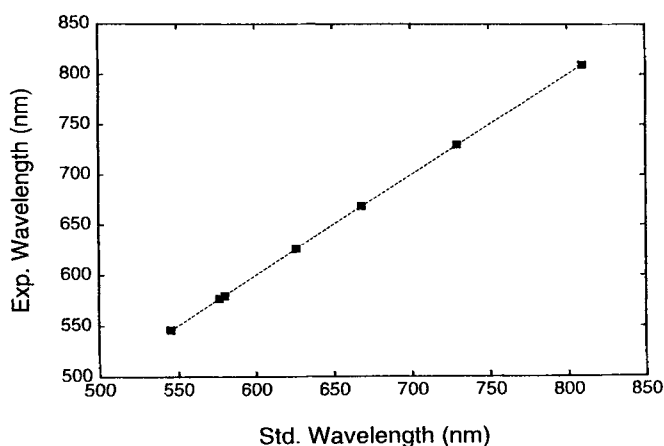


Figure 3. Plot of observed vs standard Hg peaks showing linear correlation.

It has been established by a number of workers that a natural type IIa diamond shows a sharp transition at $\sim 1332 \text{ cm}^{-1}$ (Wada and Solin 1981; Knight and White 1989). Thus our result is in excellent agreement with the reported value. From the data analysis it is also seen that the width of the peak at half maximum is 14.1 cm^{-1} .

4.2 Ruby

Ruby (Cr^{3+} doped Al_2O_3) is also an important material technologically which is used extensively for high pressure calibration, fabrication of ruby laser etc. Ruby primarily shows two lines which in our study have been found to be centred at 693.9 nm (R1 line corresponding to transition $E_{1/2} \rightarrow A_2$) and 692.5 nm (R2 line corresponding to transition $E_{3/2} \rightarrow A_2$) which correspond to 5026.18 cm^{-1} and 4996.4 cm^{-1} , respectively. The R lines of ruby are quite intense and the doublet R1 and R2 have been reported to have wavelengths 694.2 and 692.7 nm, respectively (Jayaraman 1983). The experimentally obtained peaks, deconvoluted using the 'Peakfit' package are shown in figure 5 and are found to be in good agreement with the reported values (Jayaraman 1983). The data analysis

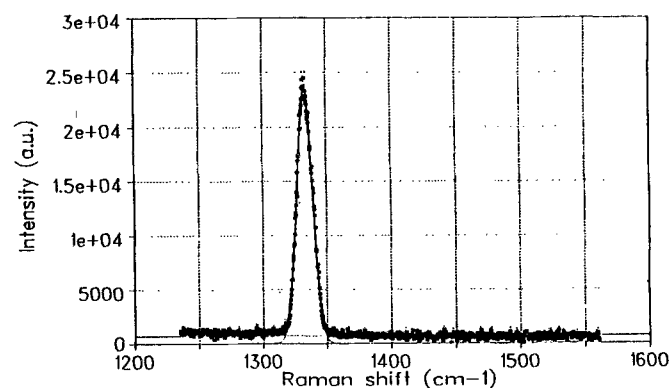


Figure 4. Raman spectrum of natural type IIa diamond crystal.

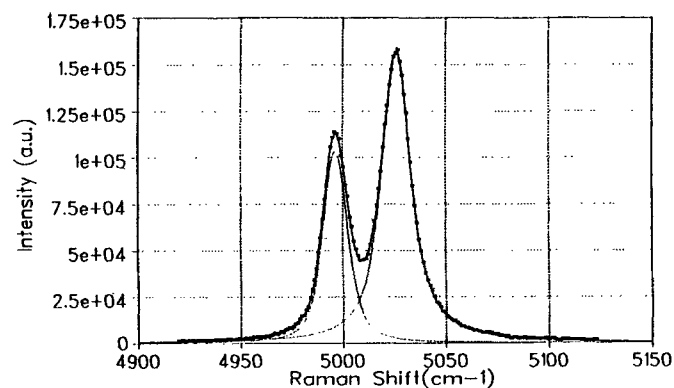


Figure 5. Raman spectrum of ruby crystal.

results yield the linewidth of R1 and R2 peaks as 16.82 cm^{-1} and 14.35 cm^{-1} , respectively.

The peak analysis results for diamond and ruby are summarized in table 2.

4.3 Benzene

Benzene has been studied in the range $750\text{--}1250 \text{ cm}^{-1}$ and two peaks centred at 992.36 cm^{-1} and 1176.8 cm^{-1} have been obtained. These peaks correspond to the fundamental vibrations of benzene as reported in literature and agree well with the reported peak positions at 992 and 1178 cm^{-1} , respectively (Grassmann and Weiler 1933;

Gerrity *et al* 1985). The peak at 992.36 cm^{-1} corresponds to carbon-to-carbon vibration while a hydrogen bending motion is found in the vibrations of the hydrogen atoms perpendicular to the C-H bond yielding the 1176.8 cm^{-1} vibration (Hibben 1939). The deconvoluted spectrum of benzene obtained in our studies is shown in figure 6. The peak at 992.35 is found to be quite sharp with a linewidth of 15.18 cm^{-1} , while the other peak has a width of 21.62 cm^{-1} .

4.4 Carbon tetrachloride

The Raman spectrum for carbon tetrachloride depicting

Table 2. Comparison between the reported and observed Raman spectra of solid samples.

Sl. No.	Sample	Observed peak values (cm^{-1})	Line width (cm^{-1})	Reported peak values (cm^{-1})
1	Diamond	1333.10	14.10	1332
2	Ruby	4996.40(692.5 nm) 5026.18(693.9 nm)	14.35 16.82	5000(692.7 nm) 5031(694.2 nm)

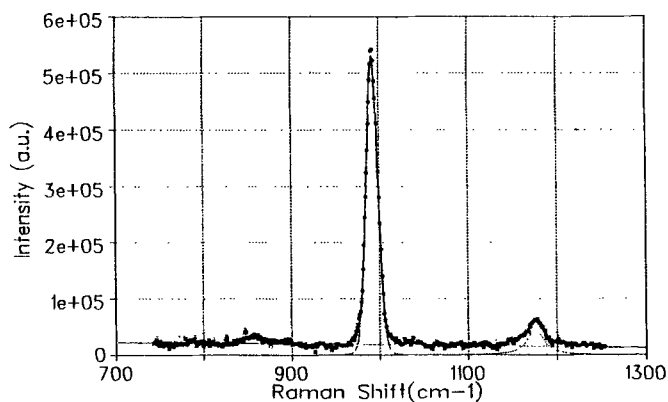


Figure 6. Raman spectrum of benzene molecule.

Table 3. Comparison between reported and observed Raman spectra of liquid samples studied.

Sl. No.	Sample	Observed peak values (cm^{-1})	Line width (cm^{-1})	Reported peak values (cm^{-1})
1	Benzene (C_6H_6)	992.36 1176.80	15.18 21.62	992 1178
2	Carbon tetrachloride (CCl_4)	218.66 313.49 458.08	19.34 21.07 20.63	218 313 458
3	Ethanol ($\text{C}_2\text{H}_5\text{OH}$)	882.43 1052.98 1095.15	19.32 27.04 32.34	883 1051 1096

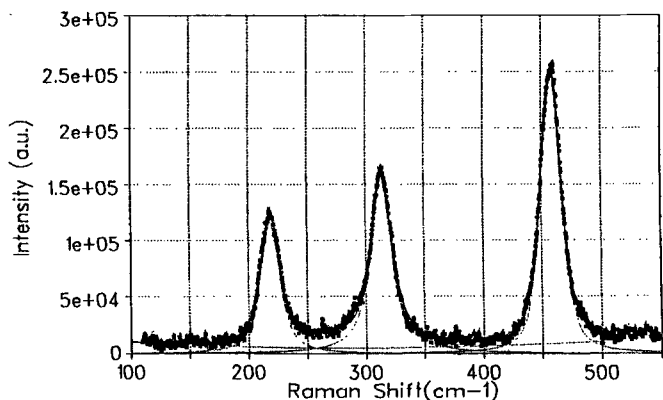


Figure 7. Raman spectrum of CCl_4 molecule.

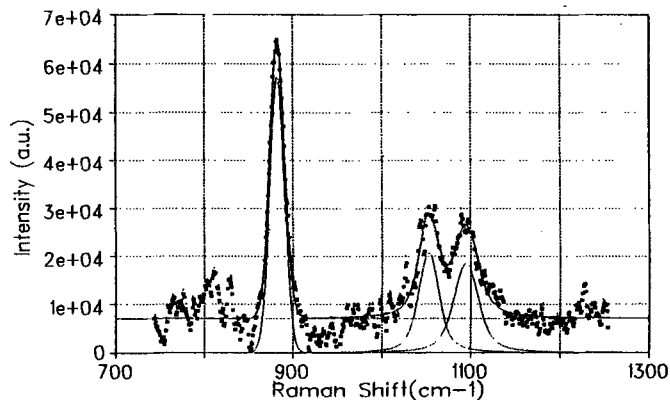


Figure 8. Raman spectrum of ethanol molecule.

deconvoluted peaks is shown in figure 7. The carbon tetrachloride molecule corresponds to a symmetrical tetrahedron (symmetry T_d). In the present study, a Raman spectra for the molecule has been obtained from 100 to 550 cm^{-1} and peaks have been observed at 218.66 cm^{-1} , 313.49 cm^{-1} and 458.08 cm^{-1} . These correspond to the fundamental vibrations of CCl_4 as reported in the literature and are quite close to the reported values at 218, 313 and 458 cm^{-1} (Hibben 1939). The observed peaks are found to be wide with peak widths of 19.34 cm^{-1} , 21.07 cm^{-1} and 20.63 cm^{-1} , respectively.

4.5 Ethanol

The Raman spectrum of ethyl alcohol has been obtained in the range 750 cm^{-1} –1250 cm^{-1} . Peaks have been observed at 882.43 cm^{-1} , 1052.98 cm^{-1} and 1095.15 cm^{-1} . These agree well with the fundamental vibrations for ethyl alcohol reported at 883, 1051 and 1096 cm^{-1} (Hibben 1939; Bolla 1934). Figure 8 shows the deconvoluted peaks for the Raman spectrum of the molecule. The linewidth for the respective peaks are 19.32 cm^{-1} , 27.04 cm^{-1} and 32.34 cm^{-1} .

The peak positions and linewidths of the liquid samples studied are summarized in table 3.

5. Conclusions

A low cost laser Raman spectrometer is described in the present study. The signal collection and focussing optics used lead to a sufficiently high resolution of the spectrometer as is evidenced by the spectra of the different samples. The high throughput of a single stage monochromator, a large grating and lower integration time required by a single channel detector also help in lowering the acquisition time. This low cost spectrometer is also being used for ultra-high pressure studies of materials using a diamond anvil cell (DAC), the details of which will be published elsewhere.

The spectra of some of the well studied solid and liquid samples are obtained. The obtained peak positions

are in good agreement with the reported peak values in the literature.

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