CONSTRUCTION OF LASER RAMAN SYSTEM USING DIODE LASER AND ITS PERFORMANCE

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ABSTRACT

We constructed a laser Raman system using a commercially available infrared diode laser. The diode laser is used without any temperature controller in a stabilized power supply. Good quality Raman spectra of sufficient wavelength resolution were obtained for a variety of chemicals and products, including solid samples. Raman spectra of several edible oils and ghee were also obtained and these were found to be largely free of fluorescence. Finally, Raman spectra of an artificial sweetener and a pharmaceutical product were obtained, showing the feasibility and reliability of the present Raman system in real-life situation.

1. INTRODUCTION

Raman Spectroscopy is now a frequently used analytical technique in a wide range of scientific, industrial, and engineering applications, such as chemical identification, process control, solid-state physics, biological research etc.[1, 2]. In a laser Raman system, different types of lasers, such as Helium-Neon laser [3], Argon ion laser, Krypton ion laser [4], Nd:YAG laser [5] are used for the excitation of Raman spectra. Recently, diode lasers with temperature controller are increasingly being employed in compact laser Raman systems [6, 7], some of which are even being commercially available [8, 9]. The diode laser Raman system has a number of advantages over conventional system using He-Ne lasers, Argon ion lasers etc. The diode laser Raman systems are extremely compact in size, do not require high voltage sources, easy to operate and are of low cost [10a].

In laser Raman systems using diode lasers, a high degree of stability of the wavelength of diode lasers is an absolute requirement. To achieve sufficient wavelength stability, usually both temperature and current control of diode lasers are required. For this purpose, active current stabilization, in conjunction with active feedback temperature control using a Peltier cooler for the diode laser housing is used. This considerably complicates the diode laser power supply and makes the laser Raman system considerably more expensive.

In this paper, we used a single-mode, MQW diode laser operating at 780 nm in the current control mode for excitation of Raman spectra in a laser Raman system designed and built in our laboratory. We examined the wavelength stability of diode laser and showed that reliable Raman spectra of good quality can be obtained from the constructed Raman system. An explanation of why an MQW structured diode laser without traditional temperature controller has excellent wavelength stability appears somewhere else [10b]. Finally, we used the system for the acquisition of spectra of some edible oils and ghee (clarified butter) and of some commercial products such as Paracetamol and sodium cyclamate.

2. EXPERIMENTAL

The diode laser used in the experimental system is a Hitachi HL7801G with a rated output power of 50 mW operating in the 780 nm range. The laser is a Multiple Quantum Well (MQW) structure having exceptional wavelength stability and is available in a 9 mm package. The package contains the laser and a monitor photodiode in a 3-pin

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configuration. The schematic diagram and the photograph of the laser are shown in Fig.1 (a and b). For mounting the diode laser, a custom-made diode laser housing is used, which also serves as a heat sink. The housing also has an adjustable focusing lens, which is used to collimate the highly divergent output laser light from the diode laser.

a   b
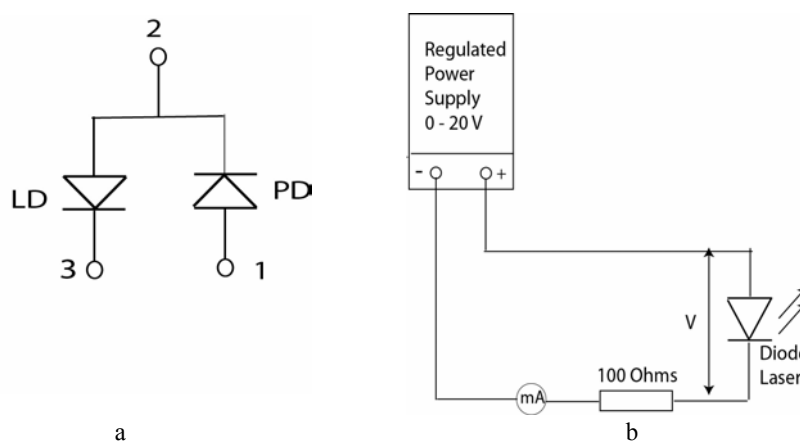
Fig. 1. (a) Internal circuit and (b) schematic diagram of diode laser circuit used for the HL7801G diode laser

The schematic diagram of the laser Raman system is shown in Fig. 2. A collimated output beam from the diode laser is directed to the sample by the 90% reflecting mirror in an oblique configuration. The sample may be a liquid in a suitable glass container or a solid in powder form. The Raman signal emitted from the sample is collected by a collection lens of 100 mm focal length (diameter 100 mm, f-number unity).
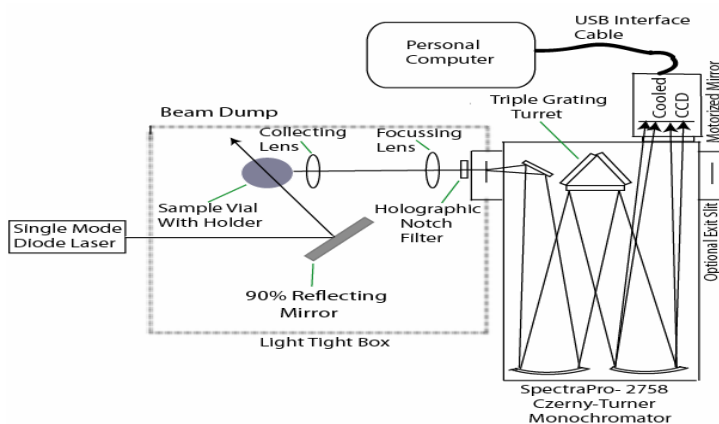
Fig. 2. Schematic diagram of the constructed laser Raman system

The collected signal is focused to the entrance slit of the spectrometer by another focusing lens. In order to exclude all stray light, which may interfere with sensitive Raman measurements, all optical components in the input side is enclosed by a light tight box. The spectrometer used is an Acton SpectraPro-2758 system in a Czerny-Turner configuration having a focal length of 750 mm. It has two ruled gratings (150 lines/mm and 300 lines/mm), which can be selected electronically. The output port of the spectrometer is equipped with an ultra-sensitive CCD camera (Princeton Instruments PIXIS100B), which captures the spectrum. The camera has a 1340X100 pixels imaging array and is cooled to -70 ^{0}C in order to reduce thermal noise. Both the CCD camera and the spectrometer are controlled by computer and by software (Winspec/32). All experiments were performed in an air-conditioned laboratory.

3. RESULTS AND DISCUSSION

We first examined the wavelength stability of the diode laser as a function of time since it is extremely important to make the laser wavelength stable in a laser Raman system. Fig. 3. shows the wavelength of the diode laser as monitored by the spectrometer as a function of elapsed time from a cold start. In the figure, we observe a rapid increase of the laser wavelength in the first minute after the laser is turned on. After that, the wavelength becomes more stable except for slight fluctuations about the mean wavelength of 781.8 nm.
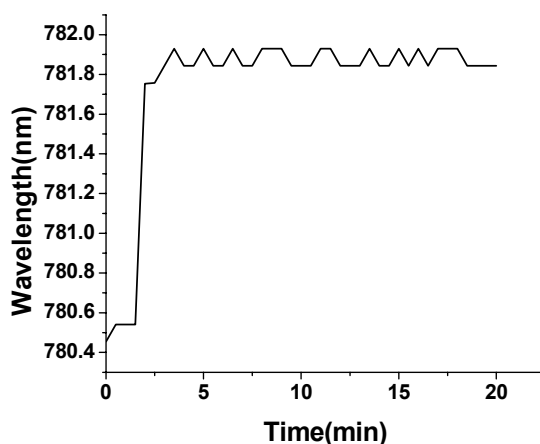

Fig. 3. Temporal dependence of wavelength of the HL7801G diode laser

After confirming the stability of the diode laser, we aligned the laser Raman system and acquired the Raman spectra of several chemicals. Fig. 4. shows the Raman spectrum of pure Benzene (Merck) integrated for a time of 90 sec. All the principal Raman lines including the 993 cm^{-1} one, resulting from the totally symmetric ring-breathing mode, are clearly observed. We carefully measured the Raman shift of each of the lines and compared them with literature values [11]. We have seen that there is a fairly good agreement of the observed Raman lines with literature values within an accuracy of about 3 cm^{-1}. This confirms the reliability and accuracy of the constructed laser Raman system using the diode laser as an excitation source.
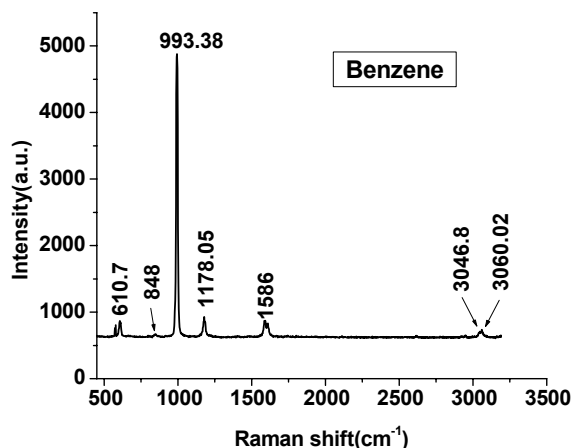
Fig. 4. Raman spectra of benzene (Merck) integrated for 90 sec using the diode laser

The use of a diode laser without any temperature controller simplifies the power supply of the diode laser. In effect, only a simple off the shelf variable voltage power supply is required unlike commercial diode laser power supplies, which require a closed loop control system using a Peltier cooler and thermocouple sensors. Even using a very simple diode laser power supply, Raman spectra of good quality and reliability can be obtained, as observed in the case of benzene.

Figures 5(a) and 5(b) show the observed Raman spectra of chemical grade toluene and glycerin. The clear Raman spectra can be observed with satisfactory match with the literature values. In case of toluene, the two closely spaced lines 1003 cm^{-1} and 1030 cm^{-1} are clearly resolved, showing that the present laser Raman system has a resolution less than 30 cm^{-1}.
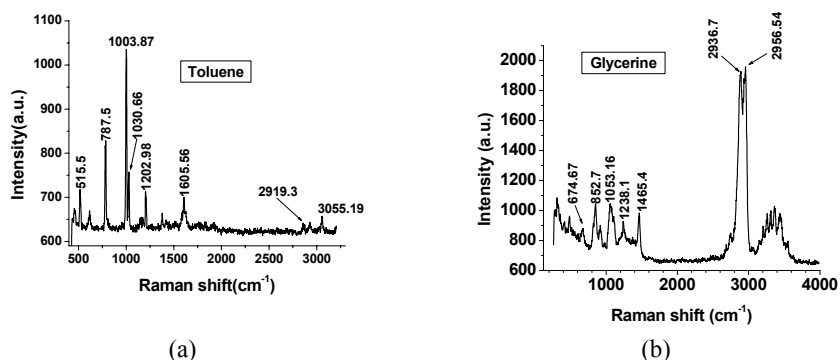

(a)

(b)

**Fig. 5.** Raman spectra of toluene and glycerin using the diode laser

Table.1.
Major Raman scattered bands typically used in Edible oil analysis.
Source: References [12-15]

| Raman Shift (cm^{-1}) (approximately)	Origin and assignments of the modes
900-800	-C-C- skeletal stretching in $-(CH_2)_n$
1100-1000	-C-C- skeletal stretching in $-(CH_2)_n$
1270	In-plane =C-H deformation (symmetric rock) in an unconjugated *cis* double bond
1305	In-phase methylene (CH$_2$) twisting motion
1440	CH$_2$ scissoring mode of the saturated fatty acid part
1660	C=C stretching mode of the *cist* unsaturated fatty acid part
1670	C=C stretching of the trans unsaturated fatty acid part
1750	C=O stretching in an ester
2855	Symmetric C-H stretching vibration of ethylene groups
2970	C-H stretching vibration of methyl groups
3015	Olefin C-H symmetric stretching vibrations of =C-H groups attributes the total instauration

Using the Laser Raman system, we acquired the Raman spectrum of many edible oils and ghee (clarified butter). The edible oils were coconut oil, ghee, soybean oil and mustard oil. The oils were collected in sealed containers from super markets to ensure the purity of the samples. The Raman spectra for these oils and ghee are shown in Fig. 6. We observed several principal Raman bands attributable to the different vibrational modes of saturated and unsaturated carbon chain in the edible oils. The identified Raman bands are shown in Table-1. By measuring the ratio of saturated and unsaturated Raman bands it is possible to measure the purity of the different edible oils [12, 13, 14].
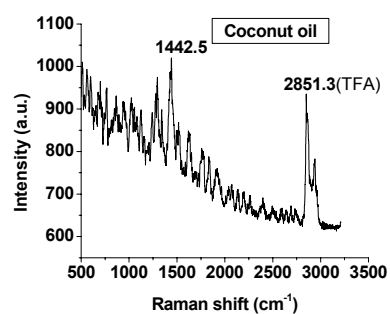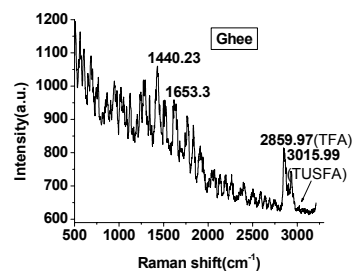
(a)   (b)
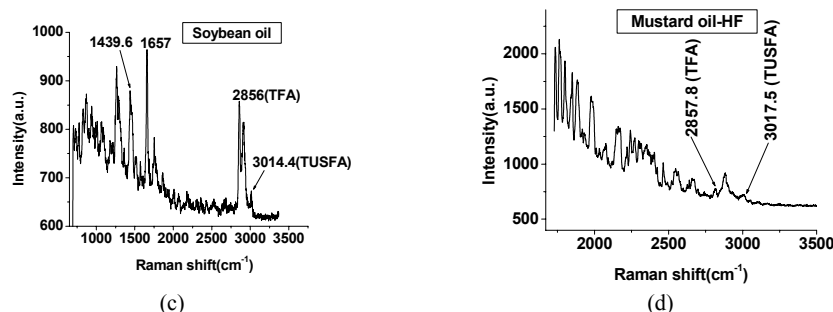
Fig. 6. Raman spectra of (a) coconut oil, (b) ghee, (c) soybean oil and (d) mustard oil using the diode laser

We observed that the Raman spectra are free from fluorescence. It is a well-known fact that many edible oils contain β-carotene and other chromophores, which emit a large amount of fluorescence and tend to mask the much weak Raman lines [15, 16]. For example, Fig. 7. shows the Raman spectra of soybean and coconut oils excited by a standard He-Ne laser at 632.8nm wavelength [17]. We observed huge amount of fluorescence in both cases, which render the Raman lines difficult or almost impossible to observe. On the other hand, by exciting with the infrared diode laser as in the present case, it is possible to largely eliminate the fluorescence and the weak Raman lines can be observed clearly.
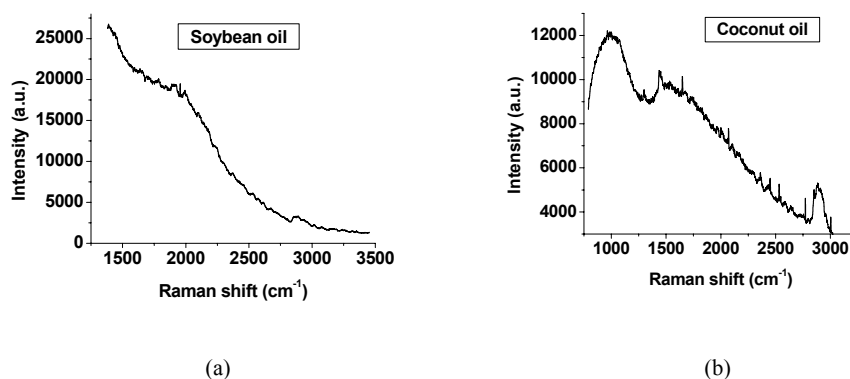
Fig. 7. Raman spectra of (a) soybean oil and (b) coconut oil excited by 632.8nm He-Ne laser

As a final example, we observed the Raman spectra of several commercial products in solid form. Figures 8 and 9 show the Raman spectra of an artificial sweetener (sodium cyclamate) and Paracetamol (napa) tablet (Para-acetyl-amino-phenol) respectively. In the case of Paracetamol tablet, it contains several compounds collectively known as excipients (dolomite, microcrystalline cellulose, talc etc.), which are added to the main ingredient to make the tablet usable. Therefore, we have collected Paracetamol in pure form (pharmaceutical grade) and have shown the Raman spectra in Fig.9(b). Figures 8 and 9 also confirm the fair agreement between our observed Raman lines and literature values [19-22].
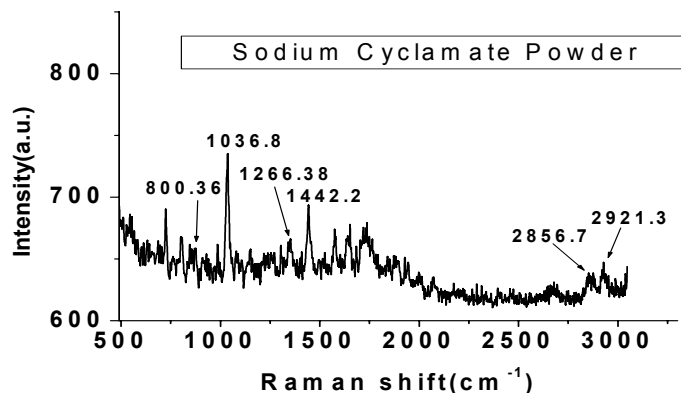
Fig. 8. Raman spectra of Sodium Cyclamate (diabetic sugar) powder
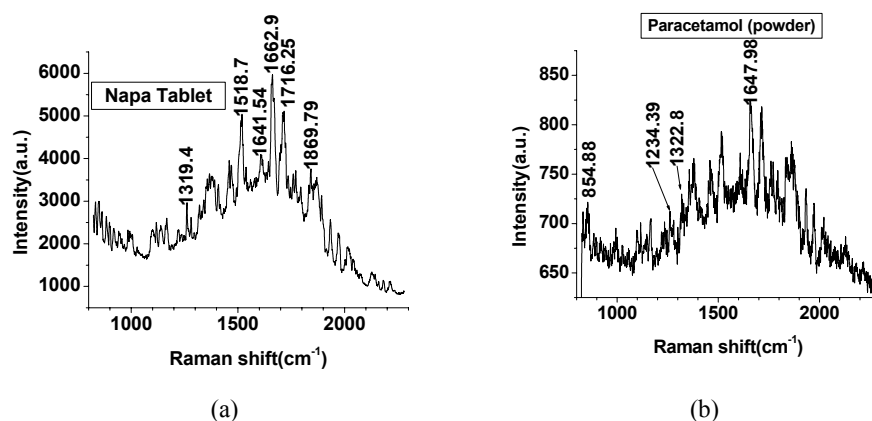

| (a) | (b) |

Fig. 9. Raman spectra of (a) Paracetamol (Napa) tablet and (b) Paracetamol powder using the diode laser

4. CONCLUSION

In this paper, we have shown that, it is possible to obtain good quality Raman spectra of many products using a simple Raman system excited by a free-running diode laser without any temperature controller. The Raman spectra are found to be free of fluorescence and are of sufficiently high resolution to identify the different vibrational modes of these chemicals. The measured frequencies of different Raman lines agree with the literature values within the experimental error and it is possible, in principle, to perform quantitative measurement on these Raman spectra.

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