Invited Paper

Micro-Mirror Arrays for Raman Spectroscopy

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ABSTRACT

In this research we study Raman and fluorescence spectroscopies as non-destructive and non-invasive methods for probing biological material and "living systems." Particularly for a living material any probe need be non-destructive and non-invasive, as well as provide real time measurement information and be cost effective to be generally useful. Over the past few years the components needed to measure weak and complex processes such as Raman scattering have evolved substantially with the ready availability of lasers, dichroic filters, low noise and sensitive detectors, digitizers and signal processors. A Raman spectrum consists of a wavelength or frequency spectrum that corresponds to the inelastic (Raman) photon signal that results from irradiating a "Raman active" material. Raman irradiation of a material usually and generally uses a single frequency laser. The Raman fingerprint spectrum that results from a Raman interaction can be determined from the frequencies scattered and received by an appropriate detector. Spectra are usually "digitized" and numerically matched to a reference sample or reference material spectra in performing an analysis. Fortunately today with the many "commercial off-the-shelf" components that are available, weak intensity effects such as Raman and fluorescence spectroscopy can be used for a number of analysis applications.

One of the experimental limitations in Raman measurement is the spectrometer itself. The spectrometer is the section of the system that either by interference plus detection or by dispersion plus detection that "signal" amplitude versus energy/frequency signals are measured. Particularly in Raman spectroscopy, optical signals carrying desired "information" about the analyte are extraordinarily weak and require special considerations when measuring. We will discuss here the use of compact spectrometers and a micro-mirror array system (used is the digital micro-mirror device (DMD) supplied by the DLP® Products group of Texas Instruments Incorporated) for analyzing dispersed light as needed in Raman and fluorescent applications.

1. NEAR INFRARED SPECTROSCOPY

Spectroscopy is any of a number of methods where the intensity of an interaction is studied versus wavelength, frequency or potential energy of the waves. Spectroscopy requires in general the generation of a "probe signal" that has frequency components corresponding to each wavelength or frequency understudy. In Raman spectroscopy however the plurality of frequency components are created within the material being probed and these bands are the so called "Raman Modes." In Raman spectroscopy a material is irradiated with an incident photon which is nearly single frequency. The energy band(s) produced by the incident photon and material "irradiation" is(are) studied spectrally. The potential energy loss or potential energy gain is the Stokes or anti-Stokes spectrum, respectively. NIR Spectroscopy is of course spectroscopy performed in the NIR region of the E/M spectrum. The NIR has several advantages relative to other regions of the spectrum. First, the solid state laser sources in the NIR region behave ideally, particularly usually exhibiting "spatial-temporal" coherence and these sources can be "mass produced." Secondly, because the NIR represents a potential energy region lower in energy than typical bond and ionization energies of the material under study, the NIR would not photochemically drive chemical bonding within most types of materials.

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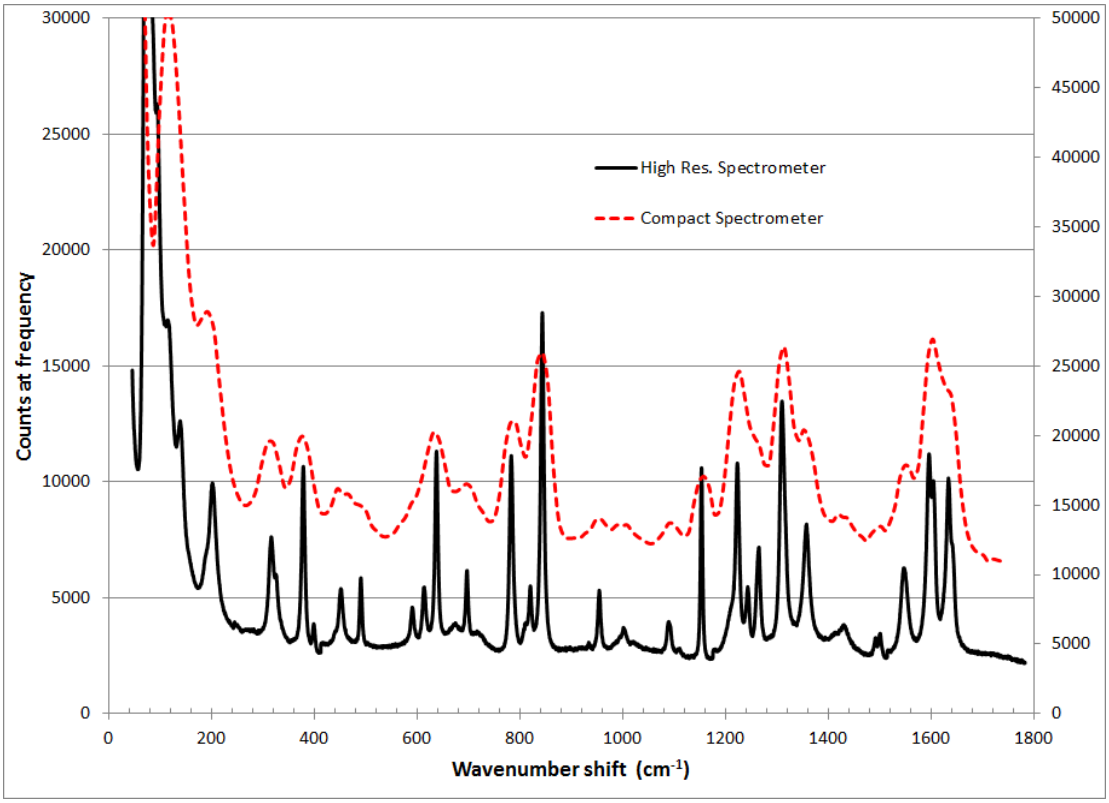


Figure 1. Acetaminophen "standard" reference spectrum using "High Res. Spectrometer" (grating dispersed UTD Gen-II) using 100 mW 785 nm excitation with 10 sec. integration time (solid line) compared to Compact Spectrometer using 400 mW 785 nm excitation with 1 second integration time (dashed line). Both spectra used "dielectric filters" to reject and filter elastic and inelastic signals.

Also, it should be noted silica fiber optics have optimum "transmission" in the NIR, and dichroic filters, lasers and detectors are all available "off the shelf" in the NIR spectral region. Finally it should be understood that inelastic scattering, that is Raman scattering is a very weak effect. Put differently, the Raman Effect has a small optical emission "cross-section." However small cross-sections can be effectively dealt with using optical engineering methodologies. Many optical systems will have trace light leaks, and nearly all systems/materials will auto-fluoresce. Methodology is needed to deal with these effects.

2. NEAR INFRARED RAMAN SPECTROSCOPY

One of the challenging experimental aspects of the Raman Effect is the spectrometer or wavelength/frequency analysis section of the analysis tool itself. The goal of our work is to demonstrate chemical imaging using Raman Spectroscopy. Many spectrometers for use in the Raman application have very large physical sizes (3/4 to 1 meter in length for example). Although not exhaustive but a list of "North American" "Hand Held" or small table top Raman spectrometers give us about a dozen companies working in the area of "small" spectrometers and provides a "why" to do this work. The size of the analysis section of the spectrometer is very important, and the entire Raman system ideally fits into a small area can operate on battery power and has adequate built in signal processing capability for analyzing spectra. Spectra from representative Raman spectrometers at UTD are shown in **Figure 1**. In our laboratory, the Texas Computational Imaging and Photonic Systems (TCIPS) laboratory, we are interested in "organ" properties

that can be determined from spectral measurements. We have studied E/M interactions of radiation with "biological material" and have concentrated on sources of E/M radiation that have a high degree of spatial-temporal coherence and the organismal understudy can perturb this wave (1-11). The material under study can be said to exhibit the characteristic set of Raman "signals." These materials also need to interact with the irradiating wave in order to give rise to the "Raman" spectrum. Note also we are concentrating our research on E/M radiation that does not drive bond breaking. It is important that the interactions (between the irradiating wave and the material under study) carry information and can be conveniently transferred to and from the sample using light guides, a.k.a. fiber optics.

Raman spectroscopy and auto-florescence measurements are important methods for studying clinical and biochemical samples. Auto-florescence intensities and Raman intensities/efficiencies and resultant spectral characteristics can depend on a number of things including a material's chemical makeup, the materials environment, (e.g. water based, or non-polar based solvent) and can depend on a material's pressure and temperature. We believe that NIR Raman and auto-fluorescence signals in combination have the information content to study properties of living material. We would argue that any interactions (Raman or auto-fluorescence) both carry information as to the relative health or relative state of a material or organismal under study.

The characteristic properties of NIR auto-florescent and Raman scattering are both central to this work and the ability to separate these "effects" are key initial results of our research. We have focused on NIR spectrometers with "single frequency" sources, deliverable by fiber, and the signal provided by the analysis section of the spectrometer carries the "information." Source, detector and sample carries "information." The source (amplitude, wavelength and noise) and detector are nominally constant and the sample is assumed to carry the time varying "information." The "known" statistical variations of the source and detector present a good assumption.

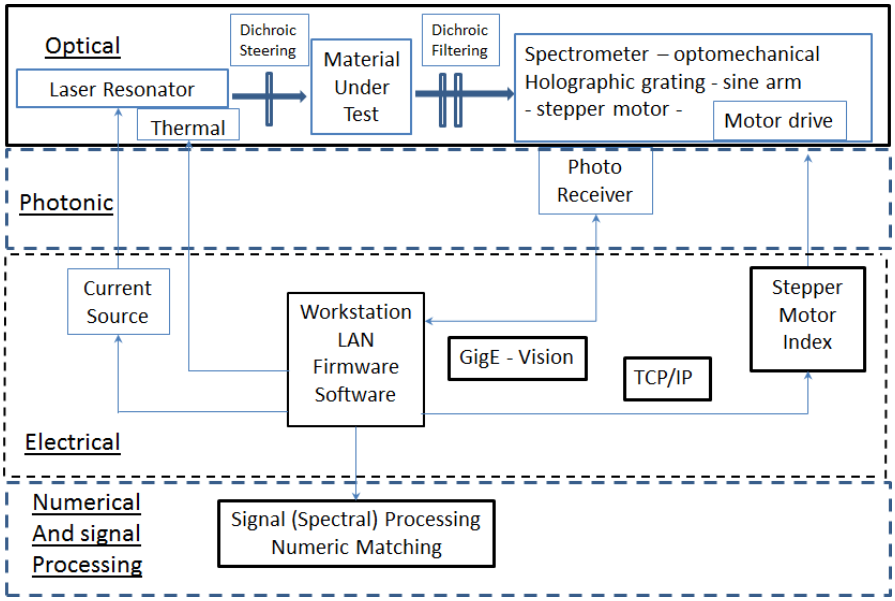


Figure 2. Raman Local Area Network (LAN) and Raman spectrometer showing All Optical, All Electronic, both optical and electronic or photonic and Signal Processing functions and "logical" layers. The section of the system enclosed in "red dot" is the "spectral analysis" section under study in this research.

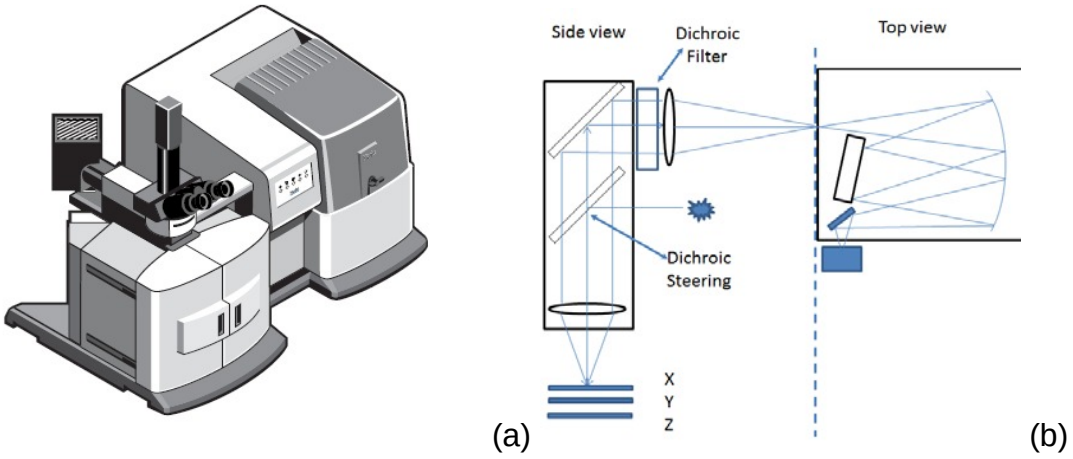
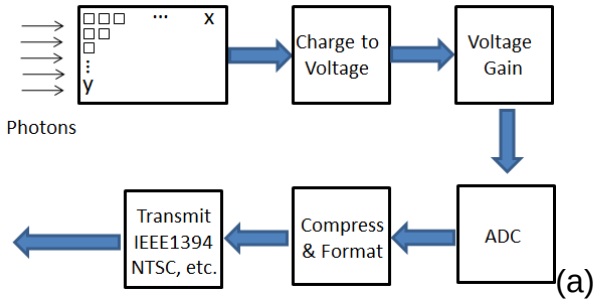


Figure 3 (a). Commercial ThermoFisher Almega holographic dispersive Raman and 3 (b). a schematic of the "GenII" Raman instrument housed in UTD CIPS lab. The use of dichroic steering and dichroic filtering is key to the UTD approach. Hologram filters are used in the commercial Almega instrument.

3. NIR RAMAN AND SIGNAL PROCESSING

Although to date we have been more interested in the Raman Spectroscopy hardware (in this research) we are also attending to aspects of the analysis that allow the correlation of signals to chemical composition as well. A compact spectrometer for evaluation of both the potential energy and the intensity of the photon is central to a correlation between experimental and theoretical data. There are two broad methods for analyzing radiation, direct measurement and interference measurements. Frequency and amplitude components of the signal carry the desired information. Shown in **Figure 2** is a schematic drawing of a "networked" Raman system that is used in the TCIPS laboratory today. The system illustrated contains optical, photonic and electrical layers or functions. These layers must communicate with each other and with the host computer.

In the TCIPS lab we have several Raman spectrometers (two instruments are shown in **Figure 3**) as well as deploy/develop hand held Raman instruments. The instrument shown in **Figure 3(a)** is a commercial instrument and finds itself very useful due to spectral flexibility and also for establishing "precise" reference spectra. The instrument shown in **Figure 3(b)** represents a research configuration embodied in our so called "Gen II" instrument and also used in this research. Spectra shown in **Figure 1** were recorded either using



Bit Depth	Max P-to-V
8	256
12	4,096
16	65,536
20	1,048,576

(b)

Figure 4(a). Graphical representation of a photon flux on a charge coupled photonic array. Photo charge is shifted and converted to a digital pattern then transferred "digitally" to the process host. Figure 4(b) shows Maximum numerical Peak to Valley values for several bit depths used in analog to digital conversion.

the Gen II spectrometer (instrument shown **Figure 3(b)**) or used a hand held spectrometer recorded with an IPS 785 nm Integrated Raman Probe with an Ocean Optics QE65000 spectrometer.

In analyzing a wave such as a Near Infrared (NIR) Raman wave, it is important to understand how the "noise" in the signal is mapped into measured signals. Optical signals have characteristic types of signal/noise. Perhaps the most challenging aspect of any spectroscopic method is the separation of the signal of interest from the noise generated by the source, material under study and detector. Noise can be treated statistically as point-to-point noise or as image noise. Transduction of optical signals from the optical domain to the electrical domain is of interest. Shown in **Figure 4** (a) is the data flow of an optical (e.g. Raman) signal. Note that once a digital signal is digitized (at the ADC in the figure) it would be very difficult to add noise under normal circumstances to the signals within the data path.

4. DIGITAL SIGNAL PROCESSING

Figure 5 illustrates the Raman spectrum recorded in this laboratory of a glucose solution in DI water together with the spectra with post digital filtering. With these spectra of compounds in aqueous solution, came our first investigations of signal processing. It should be understood that in Raman, the shifted features represent the inelastic frequency shift from the laser that is used for excitation. Although excitation of Raman signals in this case in the visible and near visible spectral regions, shifted frequencies occur in other photon energy ranges. Indeed the spectroscopist thinks in terms of wavelength shift or energy shift, the shift can be described in frequency. Hence we first used frequency filtering of the spectra applying the very standard Butterworth frequency filter. The raw Raman and the Butterworth frequency filtered data are shown in **Figure 5**. We are currently studying frequency filtering, classical transform, peak fitting and component analysis in this work in order to determine the impact of filtering, transform and fitting on analysis speed and data quality. Some transforms are better for finding periodicities whereas other transforms are preferred for extracting the frequency components themselves. Although we have used relatively straightforward approaches in data treatment here, in a future study we will research the impact of filtering and transform on the quality of data extraction.

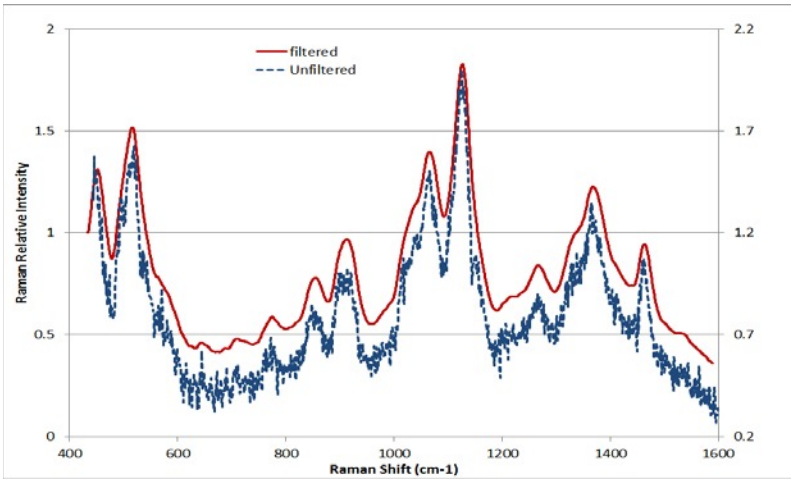


Figure 5. Raman spectrum of glucose in solution, showing both raw spectra with noise and smoothed spectra using standard Butterworth frequency filter.

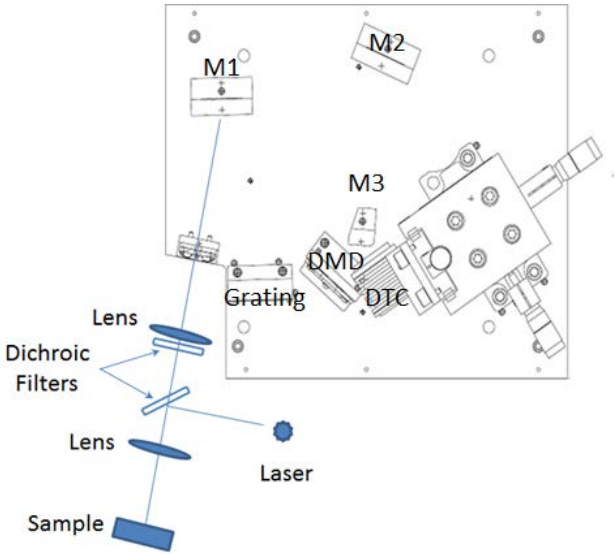


Figure 6. Adaptive reflective slit micro-mirror based Spectrometer with Raman illumination.

5. EXPERIMENT

In this research we have studied a reflective adaptive slit Spectroscopy Instrument for very low light flux Raman Spectroscopy. Obviously the spectral analysis section of the system uses a "digital mirror array" as the adaptive reflective slit as shown in **Figure 6**. The adaptive reflective slit in this application is a WXGA format DMD. Of particular importance to any of these systems is the ability to analyze light throughput in the region of the spectrum (12) where there is information as to the material under study (see **Figure 1**). We are evaluating "spectral signatures" that are centered on 850 nm where ultimately the inelastic or Raman features are induced by light injection using a 785 nm laser. In the micro-mirror based adaptive slit spectrometer configuration, the Raman spectral region is "modulated" or turned on and off using the mirror array and a grating is used to disperse the light. We are able to see significant variations in

	Strong Raman							Weak Raman						
Assume:	Source	Raman	System	DTC	Product	DTC		Source	Raman	System	DTC	Product	DTC	
	W	x-section	Thruput	A/W	Signal (A)	Noise (A)	S/N	W	x-section	Thruput	A/W	Signal (A)	Noise (A)	S/N
Source power: 125mW - 100mW	0.125							0.125						
Raman signal E-6 to E-9 (a ratio multiplier (unitless))		1.00E-06							1.00E-08					
System thruput 0.1 (a ratio multiplier			0.10							0.10				
Detector Responsivity to photon flux at a potential energy 0.65 to 0.25A/W				0.65							0.65			
Signal= I * system thruput * cross-section * Responsivity = Amp					8.13E-09							8.13E-11		
Dark = 10 pA						1.00E-11							1.00E-11	
S/N							813							8

Figure 7. Expected "in band" S/N for two "logical" cases, one representing a strong Raman signal (10^{-6}) and the other representing a weak Raman signal (10^{-8}) signal.

the photonic signatures in the Raman band that result in switching mirrors "all on" versus "all off." **Figure 7** shows in a tabular fashion the S/N expected in two logical geometries. Currently we are observing a 40-50% mirror array modulation of the signal from an "acetaminophen" sample reference.

6. CONCLUSIONS

The Reflective Adaptive Slit single photodiode spectrometer is a very useful approach for analyzing Raman signals in material and for chemical imaging. Particularly in a spectral range where array detectors are expensive or where array detectors cannot meet environmental specifications, the single element detector and adaptive reflective slit spectrometer is both cost effective and useful approach for analyzing spectral signals. Raman Signals observed with laser modulation likely result from the strong Raman signals originating from the acetaminophen reference.

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