UV Raman Spectroscopy: Photon Systems Directions and Approaches

A Discussion of UV Raman Spectroscopic Application of Photon Systems Deep UV Lasers
January 27, 2003

1.0 Background on UV resonance Raman spectroscopy

High levels of chemical specificity can be obtained using instrumental techniques such as Raman spectroscopy. This technique also requires no sample preparation or reagents, is non-contact, and non-destructive. Normal Raman spectroscopy is insensitive compared to fluorescence. Normal Raman spectroscopy is typically done in the visible or near IR and requires relatively large amounts of laser power. This is because normal Raman scatter cross-sections are small (10^{-30}cm^2) compared to fluorescence (10^{-17}cm^2). When Raman excitation occurs within an electronic resonance (absorption) band of a material, the scatter cross-section can be improved as much as 10^8. For biological materials such as nucleic and amino acids these absorption bands are very strong in the deep UV between about 220nm and 280nm. Nucleic acids absorb optimally around 240-250 nm while the absorption cross-section for amino acids is optimal around 220-235 nm. Diamond, nitrites and nitrates, and many other organic and inorganic materials have strong absorption bands in the deep UV and exhibit resonance enhancement of Raman bands when excited in the deep UV. Fluorescence resulting from deep UV excitation occurs in the 280nm to 370nm wavelength region.

In addition to resonance enhancement for many materials, a second major advantage of deep UV Raman spectroscopy is that no fluorescence interference exists when excitation is provided at wavelengths below about 250nm. A typical Raman spectral range of 4000 cm^{-1} occurs in less than 30nm above the excitation wavelength at 250nm. Independent of the excitation wavelength, no known material fluoresces at wavelengths below about 280nm. This provides complete spectral separation of Raman and fluorescence emission bands resulting in high signal to noise measurements and low detection limits.

A major reason that UV Raman spectroscopy has not yet found a major place in the world of analytical instrumentation has been the availability of compact, cost effective deep UV lasers. Present deep UV lasers of choice for UV Raman spectroscopy are frequency doubled argon or krypton lasers that provide a wide range of deep UV wavelengths, CW output, and single transverse mode operation. Although these are all very desirable traits for UV Raman spectroscopy, these lasers cost in the order of $100,000, consume over 12,000 W of electric power, require water cooling and are bulky and heavy. Cost is often not the major impediment to the use of these lasers. It is the lack of mobility and cost of installation and operation. Another laser of potential use for UV Raman is the 266nm, 4th harmonic DPSS laser. This laser, although attractive for some applications, suffers from fluorescence interference in many organic and inorganic materials for Raman bands above about 1200 cm^{-1}. In addition, 266nm is not an ideal wavelength for matching the resonance bands of many materials, and the peak power and low duty cycle of these lasers is problematic for probing many organic molecules without thermal or photochemical damage.

2.0 Pros and Cons of Photon Systems Deep UV Hollow Cathode Lasers

Photon Systems new family of deep UV lasers offer emission wavelengths at 224.3nm, 248.6nm, and other potential wavelengths at 260nm, 270nm and others. These lasers are the size, weight, and power consumption of HeNe lasers. And they have the following attributes:

- > 100 mW, quasi-CW output at several deep UV wavelengths (to over 500mW)
- Square wave laser output pulses with adjustable pulse width: <20 μs to >300 μs
- Pulse repetition rates up to 1kHz or more (limited by long term average power)
- Narrow emission linewidth: <3GHz, (i.e. < 0.1 cm^{-1} or <0.0005nm)
- Ultra stable frequency: <1 ppm (totally independent of temperature)
- Instantaneous warm-up from any ambient temperature: <20 μs
- No standby, preheating power or time required
- Wide ambient temperature range: $+120^0$C to -150^0C
- Compact laser tube: as small as 15cm long by 3.8cm diameter
- Compact power supply: 5cm wide x 15 cm long x 3 cm high
- Low power consumption: can be less than 1 W (can be powered by USB port)
- Low cost: OEM prices less than $3000
- Long lifetime: >2000 hours depending on usage (discussed in more detail below)
- No toxic materials

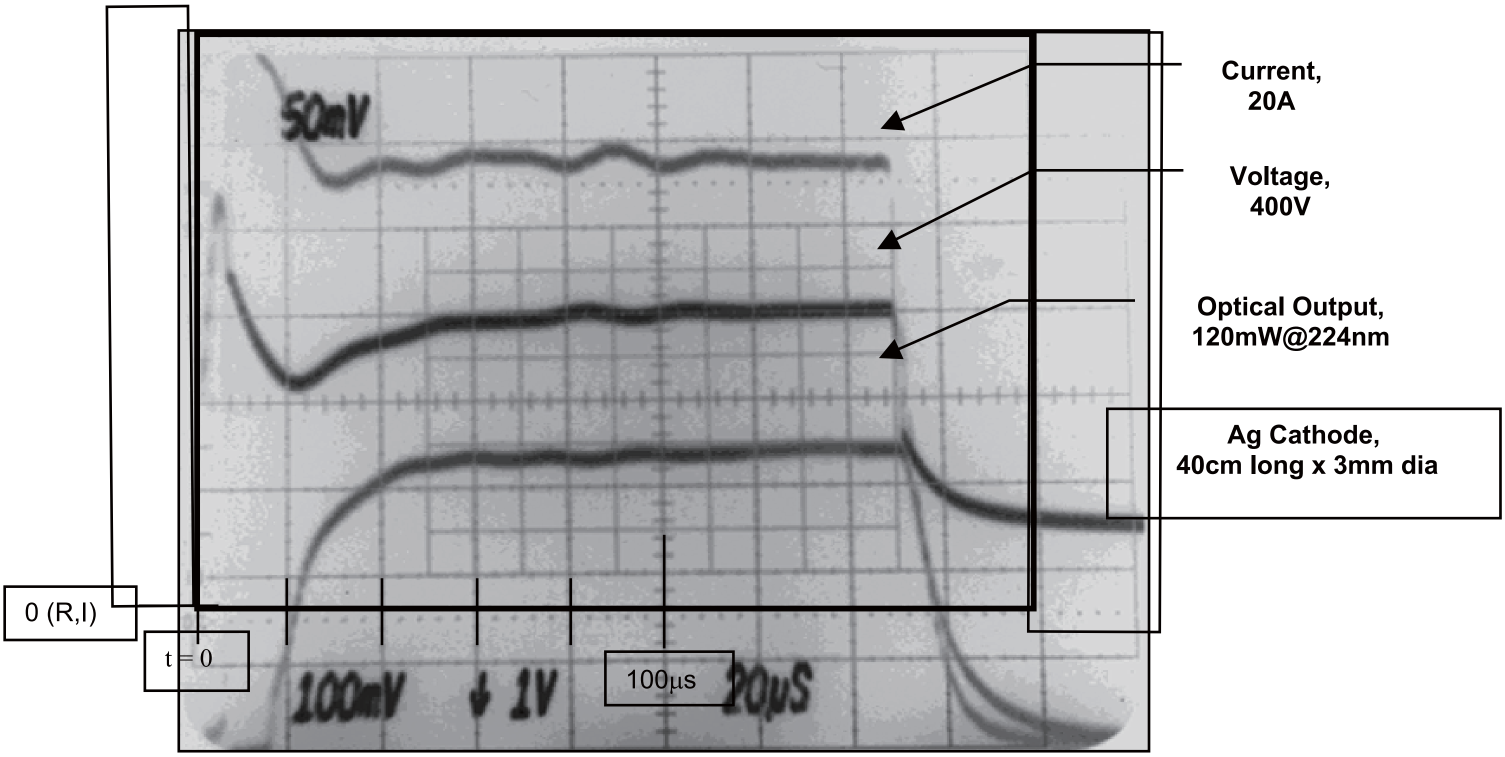
Although these lasers have many great attributes, they have limitations that include:

- Lifetime (discussed below) is pulse dependent. The lower the pulse repetition rate, the longer the lifetime.
- The "times diffraction limit", or M^2 value of the laser is about 10, which means the laser typically cannot be focused to spot sizes less than about 3 μm.
- The lasers are not true CW.

Basic Operation of HeAg and NeCu Lasers

We describe the output of our lasers as "quasi-CW" for the following reason. The laser transitions are CW transitions. This means that as long as pumping is maintained above threshold, there is laser output. Theoretically the output power can be truly CW with no interruptions for hours or months. The input power to maintain pumping above threshold and provide true CW output varies between 3kW and 10kW, depending on the laser transition. The slope efficiency of these lasers is high such that if pumping above threshold occurs, the laser output power increases rapidly. Typically output power is over 100mW at any of the deep UV wavelengths from a laser tube less than 50cm in length.

In order to keep the lasers small, simple and inexpensive, we have chosen to limit the long-term average input and output power by commutating (chopping) the input power with a duty cycle less than a few percent. Commutated operation is possible with our type of laser because of the fast time constant between application of voltage and laser output associated with our transverse hollow cathode glow discharge design. This cannot be done with positive column laser designs such as argon or krypton ion lasers, helium neon, or helium cadmium lasers. We can adjust the width of the drive power pulse to the laser tube in a range from a few μs to hundreds of μs. And we can adjust the pulse repetition rate from single pulses to over 1000 Hz. The rise and fall time of the output of the laser is typically about 15 μs to 20 μs. Electrical energy input to the laser tube in a 100 μs long pulse is about 0.5J. This is illustrated below. When a laser is operating at 1Hz, the input power is only about 0.5W. The power needed to maintain the laser above threshold during its "on" time, is supplied from a capacitor. Therefore, operation is similar to a flashlamp, except that the pulse width is controllable and more constant. We typically do not operate our lasers above about 3% duty cycle, which corresponds to a pulse repetition rate (PRF) of 300 Hz. Higher duty cycles are possible but only for limited periods of time, determined by thermal overheating of the laser tube or electronic components.



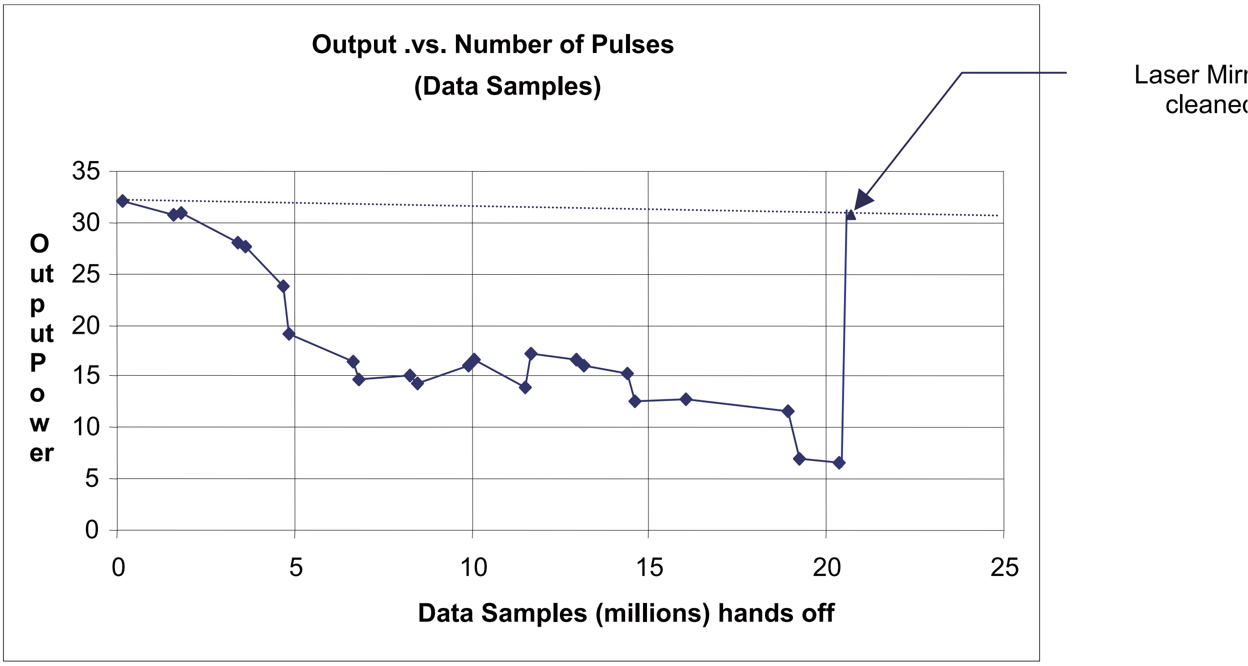
Hollow Cathode Laser Lifetime

In order to have a viable commercial product, it is our belief that the laser lifetime must exceed about one year of useful "field" use before requiring maintenance, repair or replacement. The "field lifetime" of the laser is strongly dependent on the method of use of the laser. This will be discussed below.

In our development of 224nm HeAg and 248nm NeCu lasers we have identified three basic lifetime limitation mechanisms within the laser tubes: bore erosion, buffer gas cleanup and mirror contamination. These lasers employ a hollow cathode glow discharge to form the gain medium for lasing. This technology is similar to hollow cathode lamps wherein a basic lifetime limit is related to sputter erosion of the hollow metal cathode. As metal from the inside diameter of the cathode is sputtered away, several ageing processes occur: physical change in the shape of the hollow cathode, trapping of buffer gas under the sputter deposits, and contamination of laser mirror surfaces. Each of these processes is related to the product of drive (discharge) current and time. Since our lasers are operated in a commutated fashion, the laser is kept "on" for the shortest possible time needed to make a useful measurement. This enables the longest possible operating lifetime of the laser. Operating with 100 μs pulse width at a pulse repetition frequency (PRF) of 100 Hz, the bore erosion lifetime is between about 1500 and 3000 hours. With the same pulse width but operating at a PRF of 1 Hz, the bore erosion lifetime is expected to be over 100,000 hours or essentially infinite. This corresponds to over 500 million, 100 μs wide, pulses. If the pulse width is reduced, the number of pulses is increased.

The buffer gas lifetime depends of the method of replacement of buffer gas trapped under sputter deposits. Photon Systems has two types of methods: passive and active buffer gas pressure control. In the passive method the laser tube and/or an added passive gas ballast provides the gas needed for the required lifetime of the laser. For applications where the PRF is low and data are accumulated on a single pulse basis, this passive regulation method is desirable because it is the simplest and least expensive. When higher average power is needed or more total amount of pulses are needed or required of the laser, an active buffer gas pressure regulation system is employed. In this system we sense the gas pressure and using a double solenoid valve, "burping", system we maintain the buffer gas pressure constant. The active pressure regulation system can eliminate the buffer gas lifetime issue. The passive ballast lifetime depends on the usage environment of the laser and the amount of passive gas ballast.

Mirror contamination lifetime is the primary lifetime problem with our present lasers. We have demonstrated lifetimes over 1000 hours operating at 1 Hz with a 25% degradation in output. At 50% degradation in output the lifetime is several thousand hours. Put in pulse terms, the 25% degradation point is over 3 million pulses and 50% degradation is over 11 million pulses. Output from our lifetests seems to level off after about the 50% degradation point, so it is not presently clear what the lifetime is to 25% of initial output. It may very well be over 30 million pulses. We continue to work on mirror contamination issues and believe this lifetime limitation will continue to improve with time. An example of the lifetime curve for a 248nm laser is shown below.



Lifetime (hours)	6000	3000	1200	600
Frequency	@1Hz	@2Hz	@5Hz	@10Hz

Typical laser lifetime curve for 248.6nm NeCu laser.

Photo of 9 inch, 248nm NeCu laser tube

In most cases a laser tube can be reprocessed at low cost when mirror contamination or buffer gas pressure lifetime limits are reached. This can typically be done more than 10 times before the ultimate bore erosion lifetime limit of a tube is reached. Reprocessing involves putting the laser on a vacuum process station, removing and cleaning laser mirrors, remounting mirrors and performing a vacuum reprocessing of the tube. Reprocessing time is less than one day.

Since these lasers come to full output within about 20 µs of demand for laser output, none of the laser lifetime is wasted on warm-up. Warm-up is a major consumer of lifetime of competitive laser technologies.

Hollow Cathode OEM Laser Cost

The inherent cost of these lasers is low. Basic laser tube prices can be less than $1000 with power supply cost less than $500 in OEM quantities. We believe the biggest barrier to commercial application of these lasers is not cost or price. It is making the right marriage between this laser source technology and a detection technology that is useful for some analytical instrument application. Ultimately this means using the laser at low PRF or using the laser is short bursts.

Other deep UV Laser Developments

Photon Systems is also developing deep UV semiconductor lasers under DARPA sponsorship. Our wide bandgap, InAlGaN semiconductor laser technology follows a different, more pragmatic, approach than is being followed by others in this field. We believe the commitment by DARPA is evidence of the confidence others have in our approach to deep UV semiconductor sources.

At present we cannot provide any detail of these lasers other than to say they are able to provide emission at a wide range of wavelengths from 200nm to 350nm where pure GaN emitters are unable to function. Our initial target applications are related to laser induced native fluorescence (LINF) applications because the linewidth of the early devices is not expected to be narrow enough for high resolution Raman applications. Target applications are LINF detectors in capillary electrophoresis and HPLC instruments and flow cytometers. We expect to be able to offer narrow linewidth devices for Raman spectroscopy at a future date.

3.0 UV Raman spectrometer configurations most compatible with our lasers

Photon Systems has a fundamental patent related to the use of our laser technology for UV Raman and laser induced native fluorescence (LINF) based instruments (U.S. Patent No. 6,287,869, Sept. 11, 2001, “Analytical Instrument Using A Sputtering Metal Ion Laser”). We are in the process of developing extensions of this patent and related patents regarding UV Raman and LINF instruments that employ our laser technologies.

We are presently developing several configurations of UV Raman spectrometers that are most compatible with the idiosyncrasies of our lasers. We are supported by internal funds as well as NASA and DARPA contracts. We are developing miniature, ultra-sensitive, UV Raman spectrometers that can obtain Raman data with adequate resolution based on single pulse or few numbers of pulses from our lasers. In addition to being most compatible with our lasers, using lower dosages to obtain spectra is of great interest for biological or organic samples where photochemical damage is an issue.

Typical current UV Raman spectrometers from Renishaw or JY Horiba employ FreD Ion lasers as sources. A major reason for this is the detection sensitivity, dark current and readout noise of CCD array detectors. Typical back illuminated CCD array detectors require between 6000 and 10000, 100 µs, pulses from our lasers to obtain high S/N spectra. Our lasers may be more compatible with instrument configurations similar to the Renishaw or JY Horiba instruments if they used ICCD detectors. New low light level, back thinned, back illuminated CCD array detectors expected to become available on the market soon that may be compatible with our lasers, but we do not consider the present traditional CCD arrays compatible. These new low light level back illuminated arrays are being developed by Marconi/EEV and TI.

Below is a list of UV Raman instrument configurations we believe are most compatible with our deep UV lasers.

a. Traditional scanning monochromator with single PMT detection synchronized with laser output pulses. One laser pulse for each Raman band increment. Resolution similar to traditional UV Raman instruments.
b. Traditional scanning monochromator with PMT array detector synchronized with laser output pulses. One laser pulse for each 32 Raman band increment. Spectra are stitched together in a similar fashion to the Renishaw UV Raman instrument. Resolution depends on monochromator dispersion with PMT array at 1mm pitch.
c. Traditional scanning monochromator with image intensified CCD (ICCD) array detector. The ICCD detector can presumably be replaced by low light level, back thinned, back illuminated CCD arrays when they become available.
d. Photon Systems is developing proprietary UV Raman analyzer instruments based on our lasers. These instruments are similar in size to a typical mercury lamp system used on the epi-illumination port of a standard microscope. We plan to develop this design as an accessory to standard microscopes to convert them into UV Raman microscopes.

The above configurations cover a wide range of UV Raman capabilities, size, complexity, and cost. Although we are involved in work on all of these configurations, we have the greatest interest in the ultra-miniature, low cost, limited or single purpose instruments for wide scale field or factory deployment.

4.0 Other Instrument-Related Developments at Photon Systems

Photon Systems has developed integrated CCD array and gated PMT array detection hardware and software to be used in conjunction with our hollow cathode lasers. These are described in the attached data sheets.