



Some Important Considerations in the Selection of a Tunable UV Laser Excitation Source

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Laser technology has recently evolved to the point where tunable uv radiation can be obtained using commercially available lasers. The uv output between 217–260 nm is generated indirectly by using nonlinear optical devices such as frequency doubling and mixing crystals and/or by utilizing anti-Stokes Raman shifting techniques. For any scientist using lasers, even experts, the choices in commercial laser systems can be confusing. Because these laser systems are extremely expensive, an error in choice can result in a major scientific disaster.

Recently our laboratory embarked on a project to build an uv resonance Raman spectrometer,¹ and we began a careful search for the highest intensity commercially available laser system which would permit relatively narrow ($\sim 1 \text{ cm}^{-1}$) continuously tunable uv light (217–260 nm). At present three possible routes exist; a flashlamp dye laser tunable between 440–840 nm which is frequency doubled; an excimer laser which pumps a dye laser whose output is frequency doubled; or a YAG laser which is frequency-doubled or tripled and pumps a dye laser whose output is then frequency doubled and mixed with the $1.06 \mu\text{m}$ fundamental YAG beam.

We find that for wavelengths greater than 260 nm each of these lasers is capable of generating $>20 \text{ mW}$ (average) power because the doubling crystals used in this spectral region are highly efficient. Clearly, initial cost considerations favor a flashlamp dye laser ($\sim \$25,000$ – $35,000$) purchased from a responsible manufacturer. However, the notorious instability of laser dyes in flashlamp lasers will result in high maintenance costs (*vide infra*).

For our uv resonance Raman measurements we wished to avoid nonlinear processes such as stimulated Raman which can occur with high-peak power pulsed lasers such

as the YAG or excimer laser systems. The optimal laser excitation source would be CW. Unfortunately, this is not possible because tunable uv radiation requires nonlinear harmonic generation processes which are only efficient for high peak powers. A flashlamp dye laser represents a compromise between a CW laser and the 4–10 ns pulsed Yag or excimer lasers; flashlamp dye lasers typically have pulse widths between 0.3–1.0 μs . Indeed our previous Raman studies using a Chromatix Corp CMX-4 flashlamp dye laser tunable between 260–650 nm showed no evidence for stimulated Raman scattering.^{2,3} The CMX-4 dye laser tunability was limited to wavelengths greater than 260 nm because of the low peak power of the fundamental laser output, which derived from the 1 μs pulse width and the limited radiant power available from the flashlamps and power supply.

We attempted to achieve 217–260 nm uv generation by using a 0.3 μs high power flashlamp laser using angle tuned KB_5 and lithium formate doubling crystals. These crystals had previously demonstrated doubling efficiencies of greater than 1% in the 217–260 nm spectral region. KB_5 , for example, gave 1–10% efficiencies between 217–235 nm when pumped by a 15 kW peak power nitrogen laser pumped dye laser.⁴ Lithium formate⁵ displayed greater than 2% efficiency for a nitrogen laser pumped dye laser with an output peak power of 50 kW.

A DL 1400 Phasar Corporation 10 Hz coaxially pumped dye laser was used with a plano convex unstable resonator laser cavity. The laser wavelength was tuned using a series of three prisms mounted at Brewster's angle. The fundamental dye laser output was focused into the doubling crystals which were mounted external to the dye laser cavity. The dye laser was capable of generating ca. 1 W of average power at ca. 450 nm using Coumarin 102 dye. The peak power was estimated to be 300 kW.

We were unable to generate detectable uv power between 217–235 nm using a KB_5 doubling crystal. Attempts to generate uv between 235–260 nm were similarly unsuccessful. However, we did not exhaustively attempt to optimize all of the optical parameters such as beam profile, focusing in the crystal, etc., with the lithium formate! The lack of success in generating uv power in the 217–260 nm spectral region is probably a general phenomenon for all present generation flashlamp pumped dye lasers. However, our experiments were not aided by the unreliability of the Phasar laser.

The major problem with a coaxially pumped flashlamp laser is the poor beam quality which derives from the poor optical qualities of the laser dye solution. The

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TABLE I. Dye cost, lifetimes and concentrations are taken from the Lambda Chrome laser dye catalog. Lambda Physik Corp.

λ (nm)	Excimer					YAG				
	Dye	Lifetime (Watt hrs.)	Amplifier conc. (gm/L)	Cost/gm	Estimated cost/hr.	Dye	Lifetime (Watt hrs.)	Amplifier conc. (gm/L)	Cost/gm	Estimated cost/hr.
220	Coumarin 120	20	0.21	\$58	\$11	Rhodamine 6G	>32	0.02	\$22	\$0.07
230	Coumarin 47	6	0.50	\$20	\$30	Sulfo Rhodamine B	>32	0.02	\$40	\$0.14
240	Coumarin 102	20*	0.8	\$75	\$54	DCM	>32	0.03	\$95	\$0.45
250	Coumarin 307	20	0.70	\$52	\$34	DCM	>32	0.03	\$95	\$0.45

* Not known but taken to be similar to other coumarins.

thermal gradients and shock waves set up by the flashlamp excitation result in a spatially poorly defined beam. This factor in combination with the already relatively low peak powers which derive from the 0.3 μ s temporal laser width results in extraordinarily low harmonic generation efficiencies in KB_5 and lithium formate; these doubling crystals are significantly less efficient than the ADP and KDP crystals used above 260 nm. Increasing the fundamental power of the dye laser will not help this situation. The efficiency of doubling crystals depends upon power density while the crystal degradation and destruction results mainly from energy density.⁶ The longer pulse lengths (ca. 0.3 μ s) and poorer beam quality of a flashlamp dye laser compared to the ca. 5 ns pulses of the YAG or excimer requires a higher net input energy to achieve efficient frequency doubling. These higher energies cause destruction of the frequency doubling crystals. These factors in combination with the relatively poor efficiency and fragility of the lithium formate and KB_5 doubling crystals used in the 217–260 nm spectral region prevent generation of significant uv power using flashlamp lasers.

The excimer and YAG laser systems do permit easy uv generation (between 217–320 nm) with comparable powers and costs (\$90,000–110,000), with the excimer system about \$10,000–20,000 less expensive. Depending upon the exact spectral region considered, either the YAG or excimer system shows a superior power level. This is especially true for the 320–420 nm spectral region where the excimer based laser system displays significantly greater power than the YAG system.^{7,8}

However, we have purchased a YAG system due to a clear overriding factor. It does not appear financially practical to operate the excimer based uv laser system between 217–260 nm because of the large operating costs involved in replacing laser dyes. The difference in dye laser cost is substantial, with a maximum estimated \$55/h difference in dye cost. Our discovery of this difference in the uv, which we communicated to Mel Kronick of Quanta Ray,^{7,8} has recently initiated a heated controversy in the laser trade journal literature. Bernhardt *et al.* from Quanta Ray have calculated and compared the excimer and YAG dye costs in the near uv and visible spectral region and have agreed with us and concluded that the excimer dye costs are substantially greater than the YAG. In contrast, Hohla from Lambda Physik, a manufacturer of excimer lasers, questions these

conclusions and the data used for the calculations.⁹ Although we started this argument, we wish to get embroiled in these issues only as they relate to achieving laser output in the 217–260 nm spectral region.

The large difference in dye costs for uv operation between the YAG and excimer results because of the different way uv power is generated in the YAG system versus the excimer. Both lasers excite similar types of dye lasers. The YAG laser fundamental light at 1.064 μ m is frequency-doubled in KDP second harmonic generation crystals to 532 nm and this light excites a dye laser. Because of the large efficiencies of the KDP doubling crystals, YAG outputs of 250 mJ at 532 nm are easily obtained at repetition rates of 20Hz (5 W average power). With dye efficiencies of 20–40% for dyes in the 550–700 nm spectral region, dye output energies of 50–100 mJ/pulse are easily obtained. This dye laser output is then frequency-doubled in high efficiency (>10%) KDP crystals resulting in ca. 15 mJ doubled output from 260–350 nm. The 217–260 nm uv output is generated by frequency-mixing the doubled light with the remaining 1.06 μ m radiation of the Yag. The final output energies are about 1–2 mJ per pulse. For a 20 Hz YAG system average power levels are ca. 20–40 mW between 217–260 nm. In terms of average pulse power a ca. 15 W YAG Laser is frequency-doubled resulting in ca. 5 W of power which is used to pump a dye laser. Subsequent harmonic generation techniques result in a final conversion efficiency of ca. 1%.

In contrast, for similar 217–260 nm uv power the XeCl excimer based laser system will require 18 W of 308 nm light to directly pump a dye laser. The dye laser output between 430–520 nm is frequency-doubled with ca. 1% efficiencies to 220–260 nm uv light.

Although the final output energies are similar for the YAG and excimer, the dyes used and the concentrations required are very different. The Yag uses 5 W of average power to pump red dyes such as rhodamines which are efficient (~20–40%) and relatively photochemically stable. The excitation occurs in the lowest energy singlet states at wavelengths with high dye molar extinction coefficients.

In contrast the excimer used 18 W of 308 nm light to pump less stable, and less efficient (ca. 10%) and more expensive blue dyes like coumarins. Because these dyes show lower efficiencies they require higher concentrations. From published dye specifications from laser dye

manufacturers one can obtain the required concentrations, stabilities, and costs.¹⁰ Table I lists the dyes used for generating various uv wavelengths with the YAG and excimer laser.

The cost per hour of operation to generate a specific uv output energy can be calculated from $\$ = CWP/L$ where C is the cost per gram of dye, W is the weight of dye required per unit of dye solution, L is the lifetime expressed in joules of pump power per unit volume of dye solution,¹ and P is the energy delivered per hour by the pump laser. For the excimer and the YAG, $P = 18W$ and $P = 5W$, respectively. These are the powers required to obtain similar uv energies for the two systems.

The costs per hour indicated in Table I are calculated using lower lifetime figures for the YAG and the average of the upper and lower lifetime figures for the excimer. In general the dye lasers used for excimer and Yag pumped systems are similar; separate dye solutions are used for the oscillator and amplifier stages. The estimated costs in Table I include only the costs involved in replacing the amplifier dye solution.

The neglect of the oscillator dye costs occurs because oscillator dye degradation depends upon the exact partitioning of the pump power between the oscillator and amplifying stages. In general most of the pump power excites the amplifier stage. The oscillator's contribution to dye cost can only increase the differential in cost between the excimer and the Yag pumped systems.

The clear result is that the minimum excimer dye cost is \$11/h with a maximum of \$54/h. In contrast the minimum and maximum Yag costs are \$0.07 and \$0.45/h. Thus, the YAG based laser system appears to be the optimal choice for a high power (20 mW average power) tunable uv (220–260 nm) laser source at the present time.

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1. S. A. Asher, C. Johnson, and J. Murtaugh, "Development of a New UV Resonance Raman Spectrometer for the 217–400 nm Spectral Region." *Rev. Sci. Instrum.*, in press (1983).
2. S. A. Asher, Ph.D. Thesis, Lawrence Berkeley Laboratories Report, Number 5375, University of California, Berkeley (1976).
3. S. A. Asher, L. E. Vickery, T. M. Schuster, and K. Sauer, *Biochemistry* **16**, 5849 (1977).
4. H. J. Dewey, *IEEE J. Quantum. Electron.* **QE-12**, 303 (1976).
5. F. B. Dunning, F. K. Tittel, and R. F. Stebbings, *Opt. Commun.* **7**, 181 (1973).
6. L. Armstrong, S. E. Neister, and R. Adhau, *Laser Focus* **18**(12), 49 (1982).
7. A. F. Bernhardt, *Laser Focus* **19**(1), 94 (1982).
8. A. F. Bernhardt, R. L. Herbst, and M. N. Kronick, *Laser Focus* **18**(10), 59 (1982).
9. K. L. Hohla, *Laser Focus* **18**(12), 8 (1982).
10. Dye lifetimes are taken from the Lambdachrome dye data brochure, Lambda Physik Corp.

Subambient Infrared Spectra of Several Aminoglycoside Antibiotics

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Subambient infrared (IR) spectroscopy has been discussed in the literature,^{1–5} and this technique has been applied to sugars, mostly in the far IR region (500–5 cm⁻¹),^{6–8} but also in the 4000–33 cm⁻¹ range.⁹

The following general conclusions can be drawn from the previous reports. Three general types of improvements in IR spectra occur at low temperature: sharpening and intensification of peaks, peak separations, and peak shifts. The last phenomenon is due to changes in the fundamental absorption bands that occur with changes in temperature, whereas the other phenomena are connected with loss of thermal broadening. It has also been pointed out that in order to obtain improvements in the IR spectrum at low temperature the material studied must be crystalline. Thus improvements in an IR spectrum at low temperature are indicative of at least some degree of crystallinity.

Earlier work has also shown that because detailed spectra are obtained at low temperature compounds such as sugars are easier to identify from spectra than from those obtained at ambient temperature.⁹ Moreover, it has been demonstrated that spectra can be obtained from a carefully prepared pellet;⁴ therefore, it is not necessary to prepare materials under investigation. In addition, less time is needed for an IR spectrum at low temperature than at ambient temperature.

On the basis of the above observations and conclusions, we decided to investigate possible improvements in the low temperature IR spectra of sugar-type antibiotics. Some of these antibiotics, especially the aminoglycosides, are available only in small quantities; therefore the use of a smaller sample for low temperature IR spectra is indeed appealing. Furthermore, carbohydrates, especially oligosaccharide-type antibiotics, typically give noncharacteristic IR spectra.¹⁰ An improvement in the spectra of these antibiotics would aid in identifying them in a laboratory analysis.

For our investigations a Perkin-Elmer grating spectrophotometer, Model No. 567, was used with modification. Air Products Heli Tran equipment, Model LT-3-110, with a solid sample holder compartment, was used to cool the KBr-sample pellets. Two KBr pellets, 1 mm thick, provided the IR transparent window for the vacuum shield. The Heli Tran Model was operated according to the instrument manual and a double Deuterium was used as the liquid N₂ reservoir. Temperature

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