**Chemistry 620**
**Analytical Spectroscopy**
**Paper Specific Questions – Paper #4, Due 5/8/08**

Kukura, P.; Yoon, S.; Mathies, R.A. Femtosecond stimulated Raman spectroscopy, *Anal. Chem.* **2006**, *78* (17), 5952-5959 .

1. Compare and contrast the principles (light-matter interactions) and measurement of spontaneous and stimulated Raman signals. Include energy level diagrams in your explanation.
2. Kukura *et al*. assert that "Spontaneous time-resolved Raman spectroscopy is limited to the picosecond time domain because of the transform limit …" Explain this statement and compute the pulse width needed to collect spectra with the typical 4000 $cm^{-1}$ bandwidth.
3. While a simplified apparatus is one of the developments Kukura *et al*. envision in the future of FSRS, the most recent FSRS work from the Mathies group utilizes the system below. Explain the advantage(s) of this apparatus. Note: some system components, e.g., the "seed" laser that generates the pulses sent to the amplifier, are not shown.

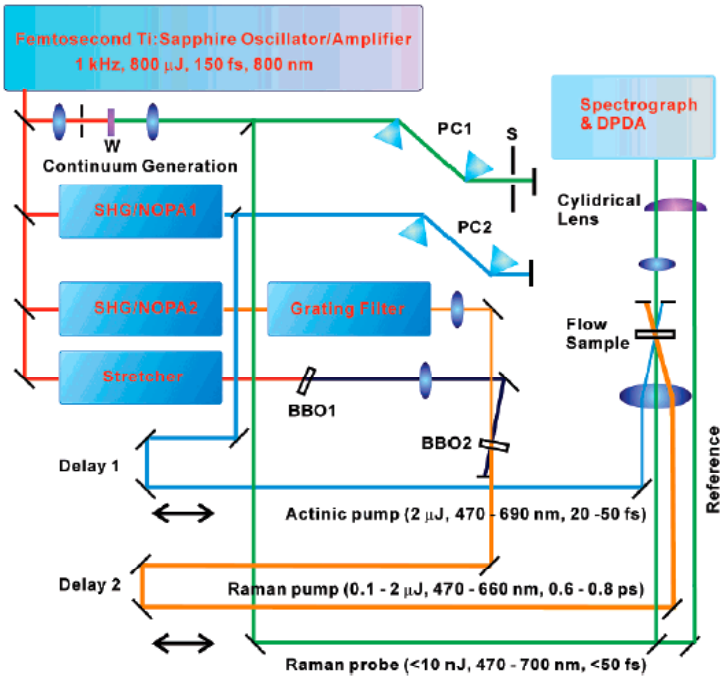


**Figure 2.** Laser system for resonance femtosecond stimulated Raman spectroscopy with a tunable visible Raman pulse (orange), a tunable visible actinic pulse (blue), and Raman probe continuum (green): W, 3 mm thick sapphire window; S, variable slit; PC1 and PC2, SF10 prism compressors; BBO1, 8 mm thick type-I BBO crystal; BBO2, 5 mm thick type-I BBO crystal; DPDA, dual photodiode array.

4. Kukura *et al*. report that the lifetime of the excited state of 11-cis-retinal in rhodopsin as <50fs. Compute how long it takes the spectrum of a species with this lifetime to decay to 1% of its initial intensity. Use your results and the data in Figure 6 to assess the accuracy of this value.
5. List any references you used to answer questions 1 – 4.