

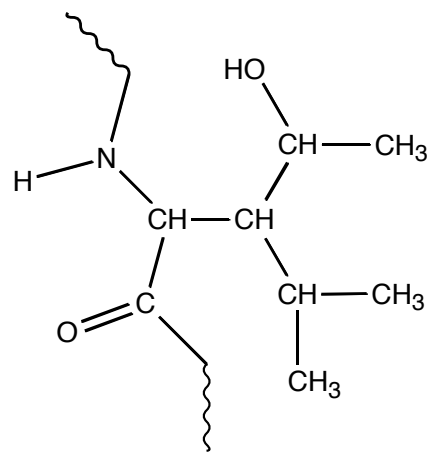
\*\* This examination is open book, but is to be worked on *independently*. You may not discuss or otherwise communicate *any* aspect of the exam with *anyone* other than C. Martin. This includes any discussions with anyone after you are done with the exam, but before the exam's due date and time. This is *very important*.

**Due in class, 9:30am, Thursday, April 10**

*Show your work for full credit. Be concise, but complete.*

*Avoid long rambling answers which indicate that you don't really understand the question.*

1. (20 points) You've just designed a cell that can express proteins with a new amino acid (this technology does exist). The amino acid is shown at right. Create a spin connectivity diagram like the kind you've seen in the hand-out (see "Amino acid spin connectivity diagrams" on the course WEB page). Try to be neat...

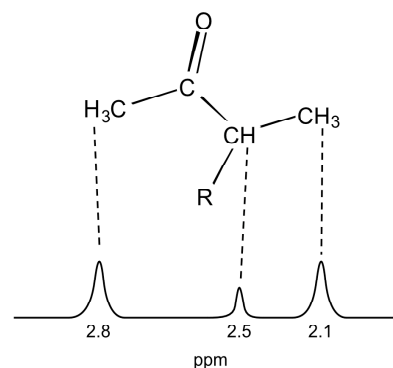


2. Consider the system at right.

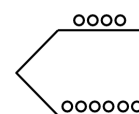
a) (10 points) Consider first, only the spin at 2.5 ppm and the following pulse sequence:



Show, on the laboratory frame spin vector diagrams below, what will happen for each value of  $\square D$  below (ie. what is the state of the **single** magnetization vector precessing at  $\square_0$  (corresponding to 2.5 ppm) immediately after the pulse sequence?). The applied field lies along the z-axis, as usual.



b) (5 points) As before, use the kind of diagram at right, to show the resulting spin population at the end of the sequence for each value of  $\square D$

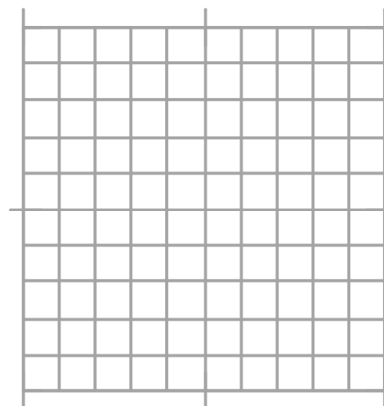


c) (5 points) Finally, show the signal (i.e., an NMR peak) resulting from an FID following the pulse sequence

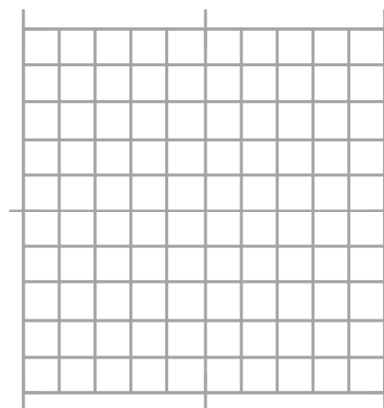
$\square D$	Laboratory Frame	Spin Population	NMR Signal
$\square D = 0$			
$\square D = \frac{\square}{2\square_0}$			
$\square D = \frac{\square}{\square_0}$			
$\square D = \frac{3\square}{2\square_0}$			
$\square D = \frac{2\square}{\square_0}$			

2 (continued)

d) (5 points) Draw a “bird’s eye” view of the resulting 2D plot one would get by Fourier transforming a set of experiments like those above with respect to first the FID time and then by the delay time  $\tau_D$ . What are the axes? Put values on the axes and place the “peaks” accordingly. Consider only the 2.5 ppm peak.



e) (5 points) Finally, now imagine all 3 resonances and assume that all 3 undergo the same  $90^\circ$  pulses (but each has its own  $\tau_D$ ). What might the above plot look like now? Think about inter-peak interactions. Explain.



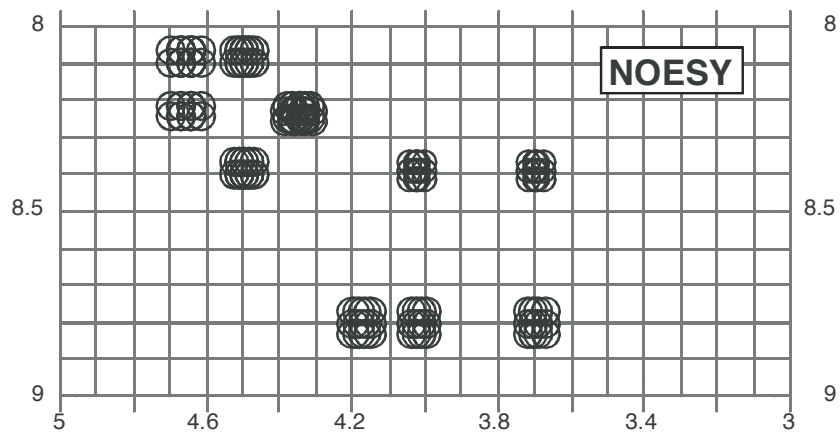
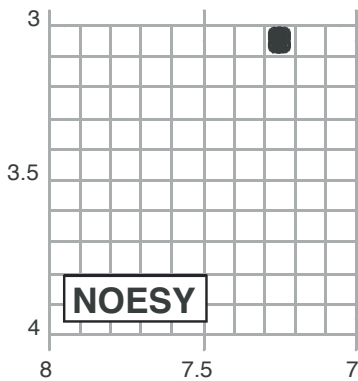
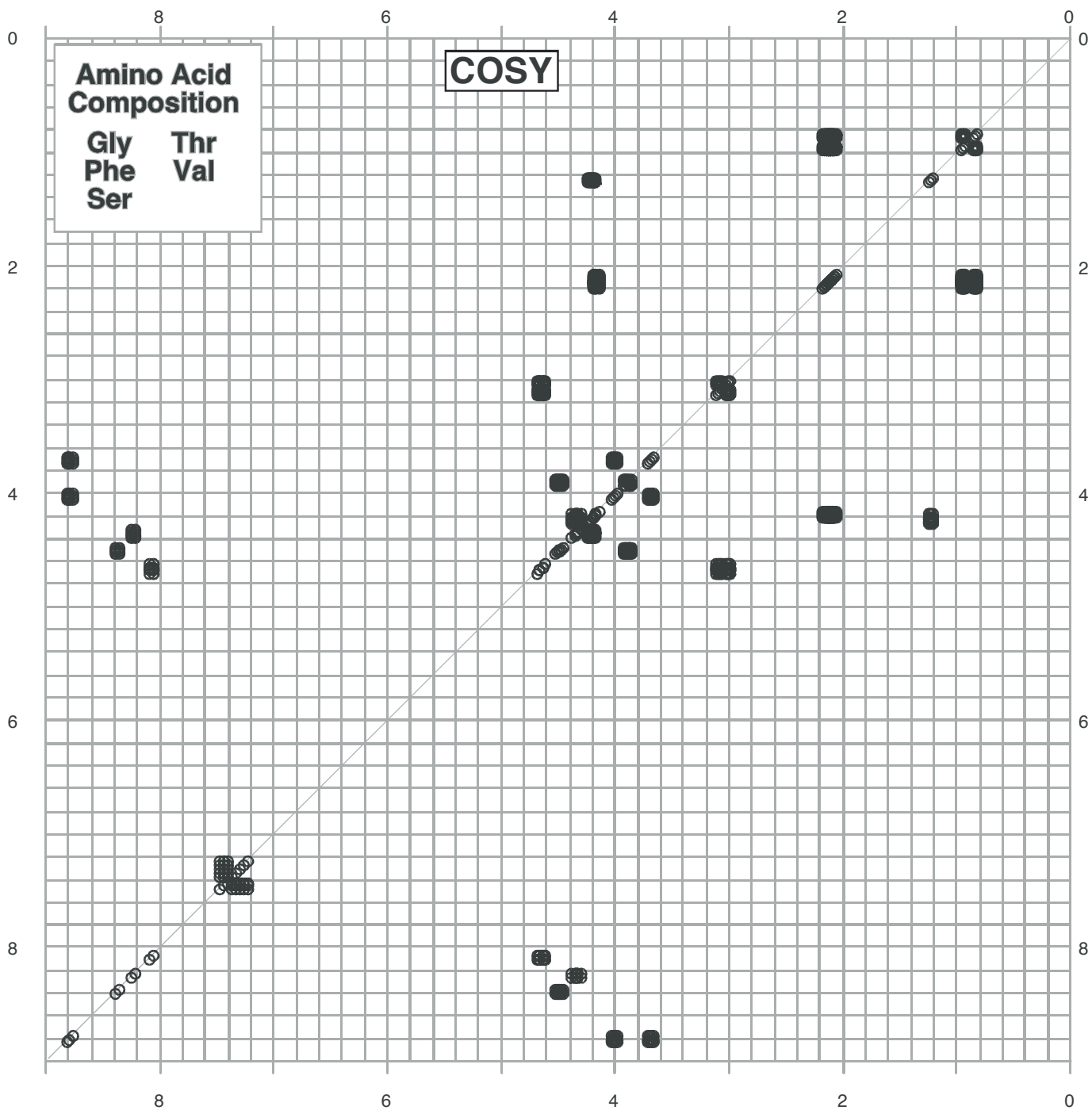
3. On the accompanying page, you will find COSY and NOESY NMR spectra of a pentapeptide. The composition of the peptide is one each of Gly, Phe, Ser, Thr, and Val. Assign each of the peaks in the spectra and then answer the following questions.

a) (25 points) On the answer sheet that follows the spectra, indicate the approximate chemical shift for each proton. If a class of protons is inequivalent, indicate the multiple chemical shifts values as follows "3.52/3.64." If you cannot determine the chemical shift of a proton, indicate so and explain why.

b) (10 points) Place the sequence of the peptide on the answer sheet that follows the spectra

c) (10 points) Near the diagonal, there is a cluster of barely off-diagonal peaks near 3.0-3.1 ppm. What are these off-diagonal peaks?

d) (5 points) Explain the peak in the NOESY spectrum blow up at lower left (near the intersection of 3.05 and 7.25 ppm).



Name: \_\_\_\_\_

Peptide Sequence:

NH<sub>2</sub> - \_\_\_\_\_ - \_\_\_\_\_ - \_\_\_\_\_ - \_\_\_\_\_ - \_\_\_\_\_ - COOH

Chemical Shift Assignments

