

Chemistry 416 “Spectroscopy”  
Fall Semester 1993  
Dr. Rainer Glaser

**The “Spectroscopy” Final**

Tuesday, December 14, 1993

7:40 - 9:40 am

Hand-out: 12/13 at 11 am; Collect: 12/14 at 9:40 am

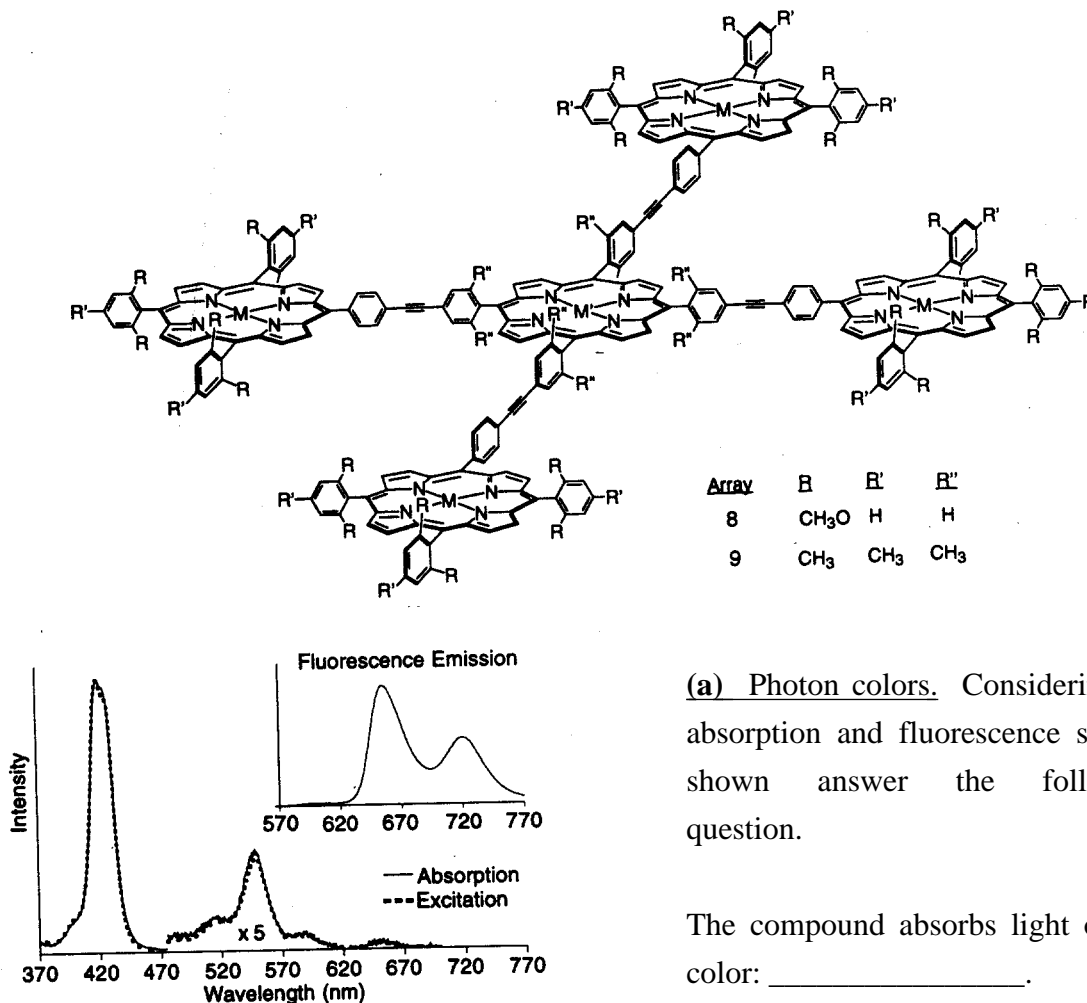
Name:
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Question 1 (UV)	30	
Question 2 (Mass Spec.)	30	
Question 3 (NMR Basics)	40	
Question 4 (NMR Relax.)	32	
Question 5 (1-D-NMR)	38	
Question 6 (2-D NMR)	30	
Total	200	

**Question 1.** Building Block Synthesis of Porphyrin Light-Harvesting Arrays.

(Prathapan, S.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7519-7520. See also: *Science* **1993**, *261*, 1388-1389.)

Photosynthetic organisms employ light-harvesting complexes to capture dilute sunlight and funnel energy to the reaction centers. Understanding light harvesting phenomena at the molecular level is a major objective of photosynthesis research and might also provide the foundation for the design of synthetic molecular devices. The authors synthesized the pentamers shown. The absorption and emission spectra of pentamer **8**, where M=Zn, are shown in Figure 1.



**Figure 1.** Absorption, fluorescence excitation ( $\lambda_{em}$  721 nm), and fluorescence emission ( $\lambda_{em}$  421 or 547 nm) spectra of **8** in CH<sub>2</sub>Cl<sub>2</sub> at 303 K. The weak fluorescence of the zinc porphyrins (601, 648 nm; assumed 1:4 ratio) is partially obscured by the fluorescence of the core free base porphyrin (656, 721 nm). The absorption and fluorescence excitation spectra were fitted by normalization at the Soret bands.

(a) Photon colors. Considering the absorption and fluorescence spectra shown answer the following question.

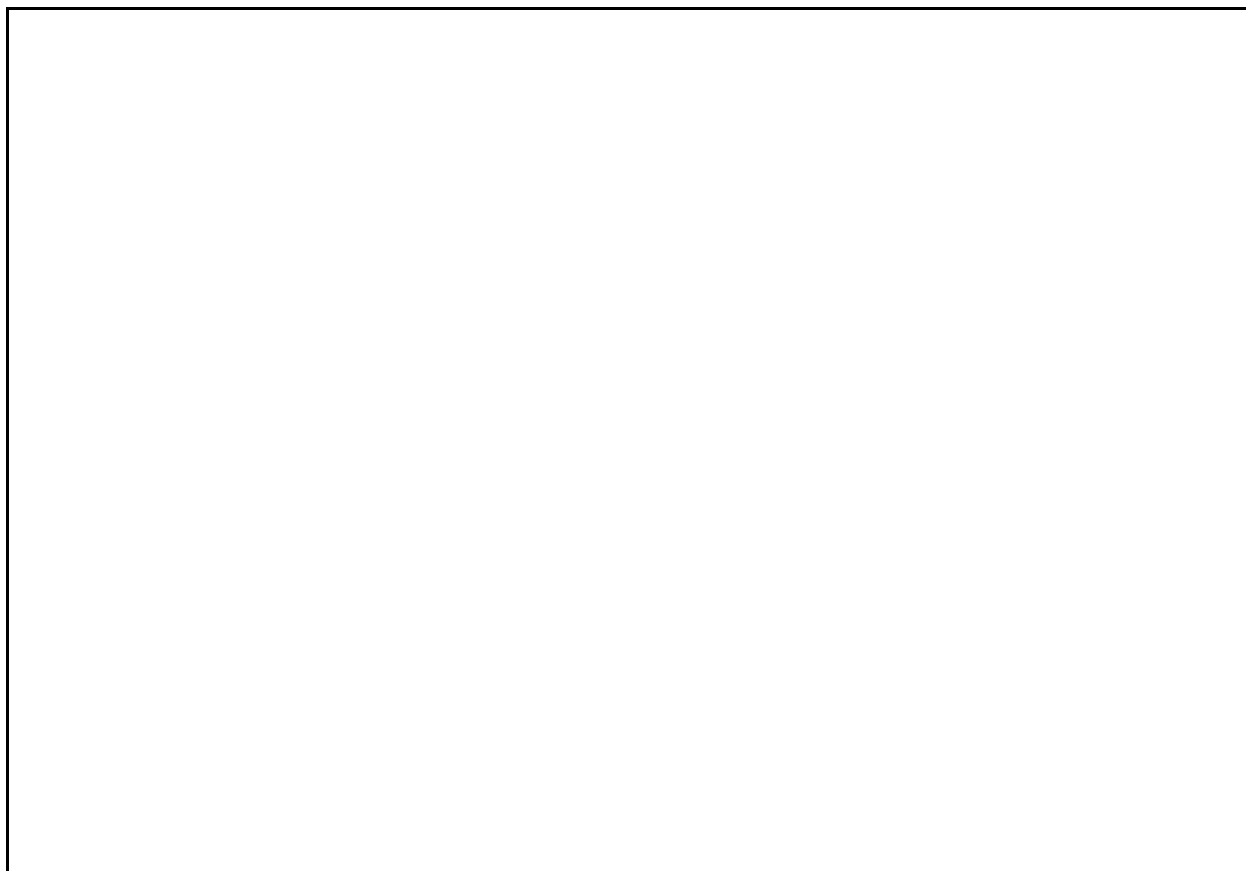
The compound absorbs light of this color: \_\_\_\_\_.

The compound emits fluorescence light of tcolor: \_\_\_\_\_.

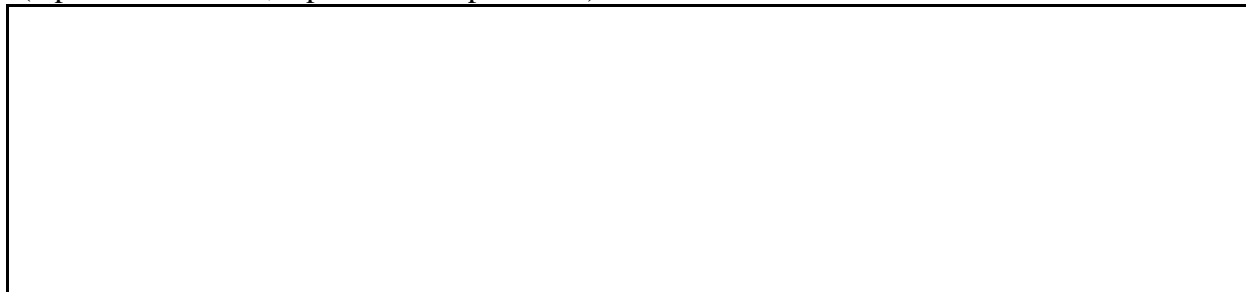
Compound's color is: \_\_\_\_\_.

(2 points each blank)

**(b) Schematic State Diagram.** Use a schematic energy diagram that shows the ground state and the various relevant excited states that play a role in the absorption and in the fluorescence. Identify the transitions associated with absorption and fluorescence and show them as arrows. Indicate all other non-emitting transitions between states and give their respective names. Note: Consider the scenario for two absorption and two emission bands. (18 points)



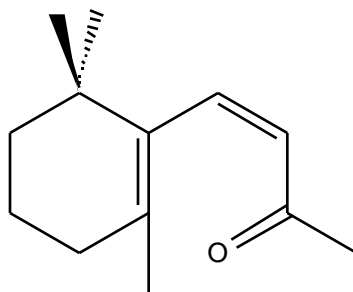
**(c) Solvent Effects.** Discuss qualitatively the changes that you would expect in the absorption and in the fluorescence spectra if you were to *change to a more polar solvent*. Explain briefly why you would expect the \_\_\_\_\_ (positive, negative) \_\_\_\_\_ (term for solvent effects on UV spectra) to be so much \_\_\_\_\_ (more, less) for the fluorescence bands. (1 point each blank, 3 points for explanation)



**Question 2.** Mass Spectry: GC-GC-MS-MS.

(Claude, S. G. et al. *Analysis of Complex Mixtures*, in *Advances in Mass Spectroscopy*, Vol. 11B, Longevialle, P., Ed.; Heyden & Son, London, **1989**, p. 1278.)

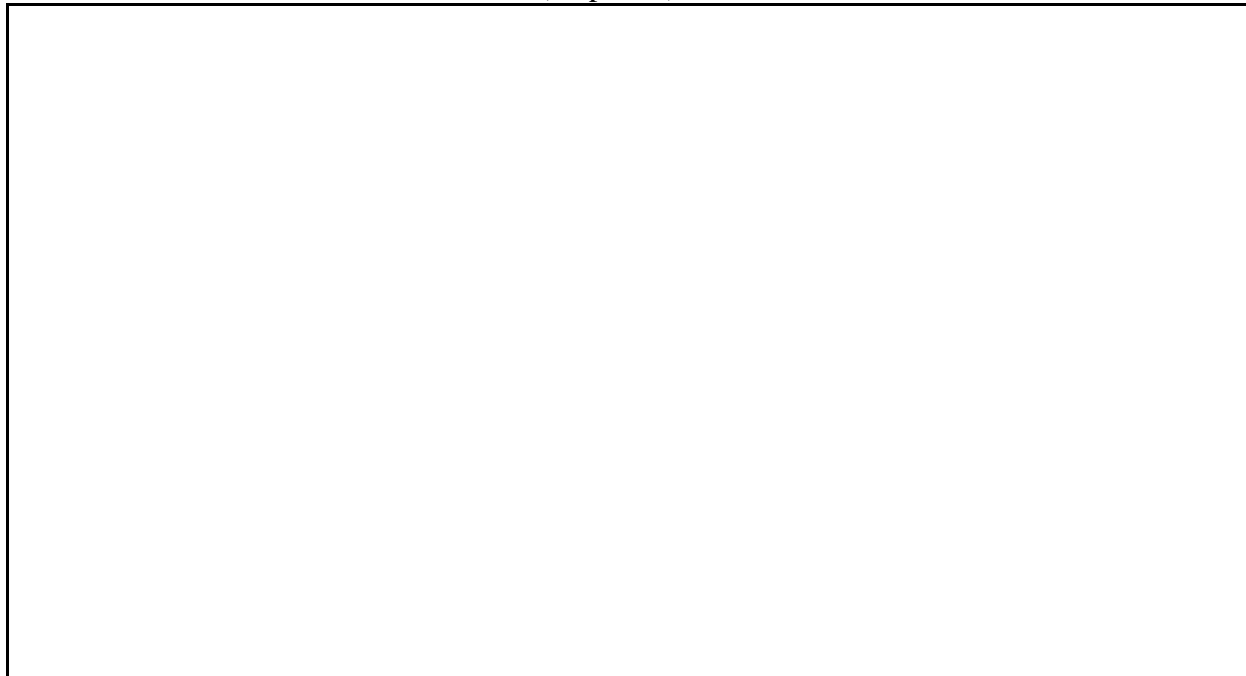
The analysis of complex mixtures requires high resolution chromatographic separation and even the use of very efficient columns cannot prevent the overlap of certain peaks. In order to overcome this difficulty, the authors built a simple multi-column system that is connected to an MS-MS instrument. With this instrument, it was possible to separate  $\alpha$ -ionone from the essential oil *Buddleia salvi-folia* and to determine its fragmentation reactions. Let's look at the fragmentation reactions of this unsaturated ketone.



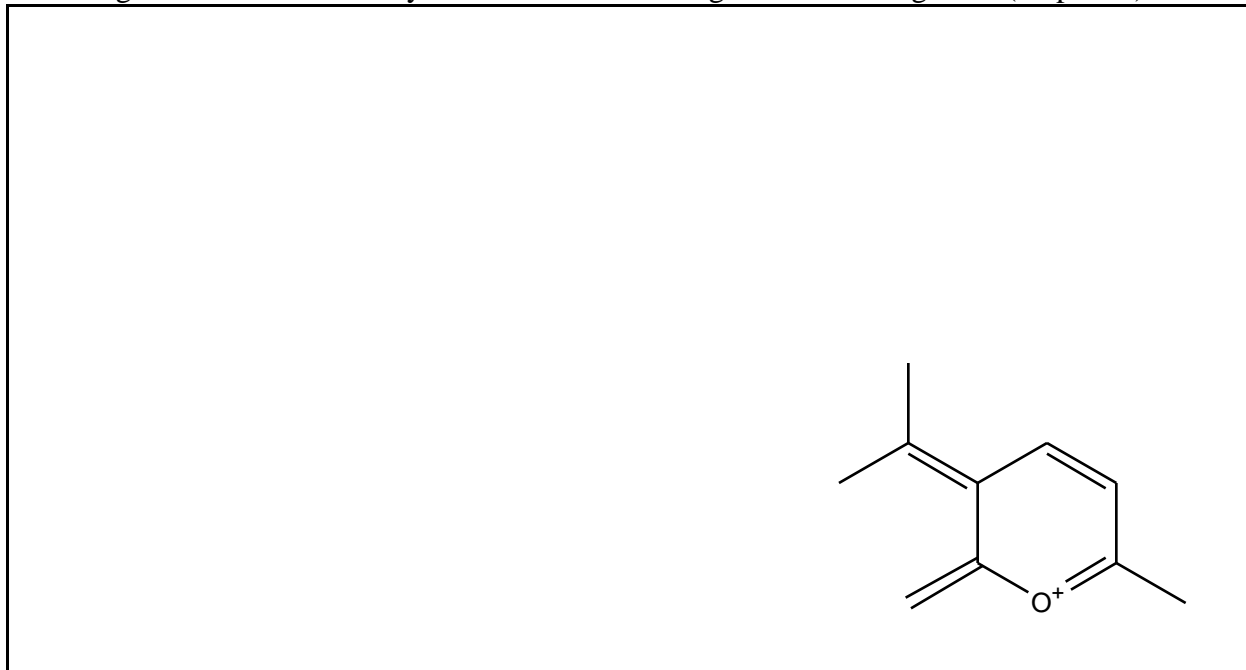
$\alpha$ -ionone,  $m = 192$

(a) Draw the parent ion of  $\alpha$ -ionone ( $m/z=192$ ) and clearly indicate the location of the charge. Show all electrons. This parent ion may fragment via the elimination of  $C_2H_4$  forming a cation with  $m/z=164$ . Suggest a structure for the ion  $m/z=164$ . (10 points)

(b) -Cleavage of the parent ion leads to an ion with  $m/z=177$ , that is, -cleavage eliminates a \_\_\_\_\_ radical. Ion  $m/z=177$  then eliminates  $C_2H_4$  in a fashion similar to (a) to give ion  $m/z=149$ . This ion  $m/z=149$  loses \_\_\_\_\_ to form the ion  $m/z=121$ . Show the structures of the ions with  $m/z$  177, 149, and 121. (10 points)

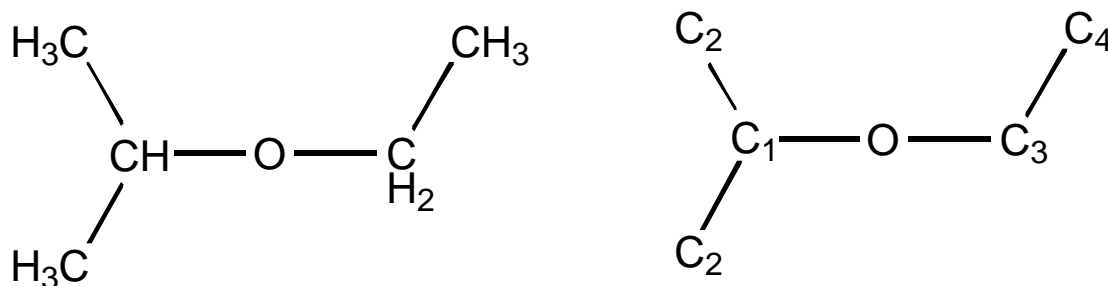


(c) In a third route of fragmentation, the ion shown with  $m/z=149$  is produced. Provide a mechanism for the formation of  $m/z=149$  from the parent ion of -ionone. Indicate bond breakings with arrows. Clearly show what neutral fragments are being lost. (10 points)



**Question 3.** Chemical Shifts, Coupling Constants and Multiplicities.

Let's look at the simple ester shown below. We will be using this ester quite a bit in the following. We'll start really easy and then get into it more deeply. In the following, always refer to the numbering shown on the right. The H atoms attached to C<sub>1</sub> will be called the H<sub>1</sub> atoms and so on.



(a) The <sup>1</sup>H NMR spectrum.

Using Table \_\_\_\_\_ from Pretsch, Clerc, Simon, and Seibl, provide the chemical shifts for the H-atoms. Give the multiplicities (e.g. singlet, doublet ...) assuming that there is no long-range coupling over the O-atom. Then draw the spectrum in the box below and give the relative intensities of the multiplet lines. (1 point each blank, 5 for spectrum and intensities = 15)

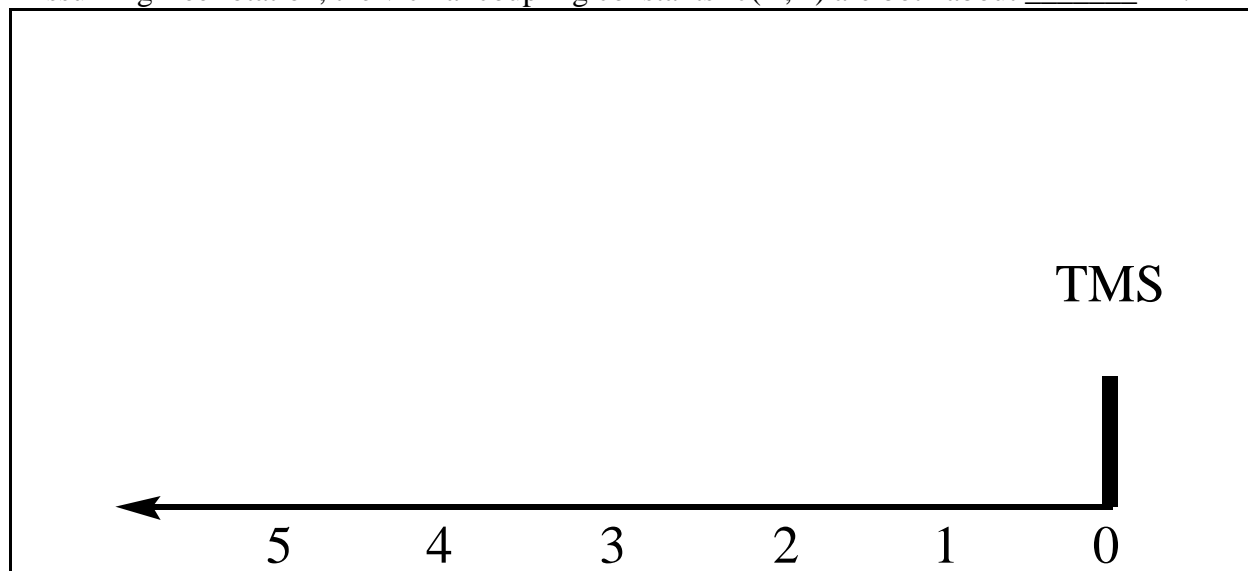
Chemical shift of H<sub>1</sub> is \_\_\_\_\_ ppm and the multiplicity is \_\_\_\_\_.

Chemical shift of H<sub>2</sub> is \_\_\_\_\_ ppm and the multiplicity is \_\_\_\_\_.

Chemical shift of H<sub>3</sub> is \_\_\_\_\_ ppm and the multiplicity is \_\_\_\_\_.

Chemical shift of H<sub>4</sub> is \_\_\_\_\_ ppm and the multiplicity is \_\_\_\_\_.

Assuming free rotation, the vicinal coupling constants <sup>3</sup>J(H,H) are both about \_\_\_\_\_ Hz.



(b) The BB-decoupled  $^{13}\text{C}$  NMR Spectrum.

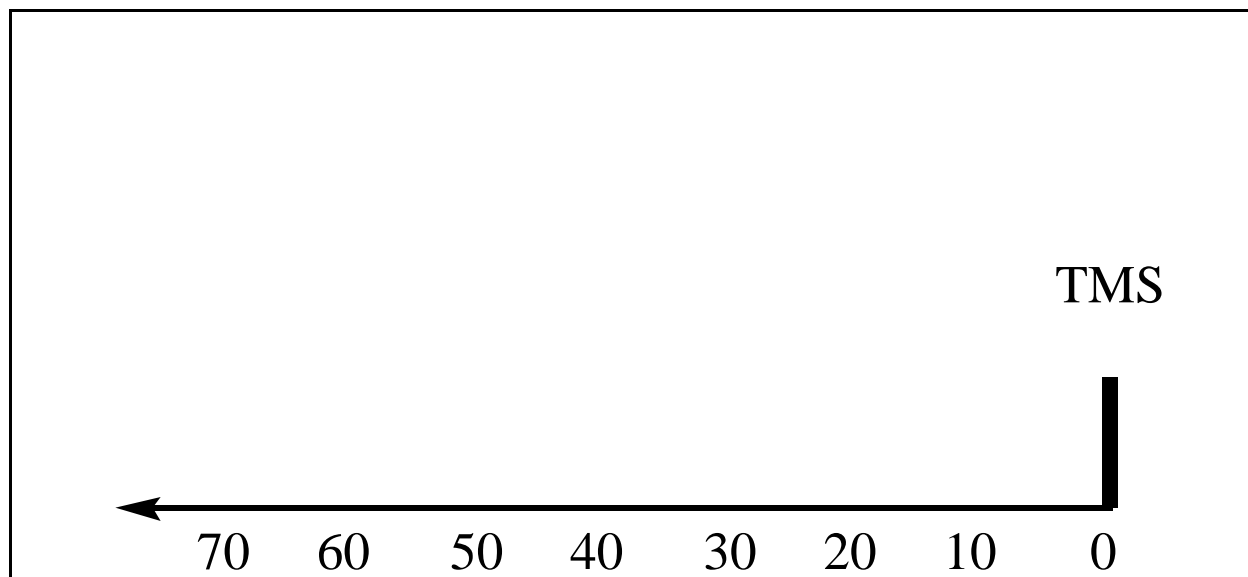
Using Table \_\_\_\_\_ in Pretsch, Clerc, Simon, and Seibl, provide the chemical shifts for the C-atoms. Then draw the spectrum in the box below. (1 point each blank, 2 for spectrum = 7)

Chemical shift of  $\text{C}_1$  is \_\_\_\_\_ ppm.

Chemical shift of  $\text{C}_2$  is \_\_\_\_\_ ppm.

Chemical shift of  $\text{C}_3$  is \_\_\_\_\_ ppm.

Chemical shift of  $\text{C}_4$  is \_\_\_\_\_ ppm.



So, that's the basics. Now we can start with the real stuff.

(c) Coupled  $^{13}\text{C}$ -NMR Spectra. (1 point each blank, 4 points each section next page = 18)

If we just had the BB decoupled spectrum, it would not be possible to assign the two C-resonances around 65 ppm. Right? To make that assignment, we need to know the numbers of H atoms attached to each of these signals. Let's consider C(3). C(3) couples to the directly attached H-atoms with a coupling constant of  $^1\text{J}(\text{C},\text{H})$  of about \_\_\_\_\_ Hz. The influence of the proximate O atom makes this  $^1\text{J}(\text{C},\text{H})$  value a bit \_\_\_\_\_ (larger, smaller) compared to the typical  $^1\text{J}(\text{C},\text{H})$  value for an  $\text{sp}^3$  C of \_\_\_\_\_ Hz. The C(3) also couples with the H-atoms of the attached methyl group. The \_\_\_\_\_ (geminal, vicinal)  $^2\text{J}(\text{C},\text{H})$  value is about \_\_\_\_\_ Hz. Thus, the C(3) signal will show up as (give description of the fine splitting) \_\_\_\_\_ . That is quite a few lines. We almost never ever record  $^{13}\text{C}$  spectra with the full H-coupling. Rather we will use some form of H decoupling technique. Let's compare the BB decoupled spectrum with the commonly used off-resonance and the gated decoupling spectrum. Repeat your drawing from (b) and draw the other spectra relative to it clearly indicating the differences. Answer question with "yes" or "no".

**BB decoupled  $^{13}\text{C}$  spectrum.**

Gives chemical shifts:	Gives $^1\text{J}(\text{C,H})$ values:
Decoupler on before acquisition:	Decoupler on during acquisition:

**Gated decoupled  $^{13}\text{C}$  spectrum.**

Gives chemical shifts:	Gives $^1\text{J}(\text{C,H})$ values:
Decoupler on before acquisition:	Decoupler on during acquisition:

**Off resonance decoupled  $^{13}\text{C}$  spectrum.**

Gives chemical shifts:	Gives $^1\text{J}(\text{C,H})$ values:
Decoupler on before acquisition:	Decoupler on during acquisition:



**Question 4. Relaxation.**

We are still looking at the ether shown in Question 4. All nomenclature as above.

**(a) Inversion Recovery Method.**

Let's look just at the relaxation times  $T_1$  of the carbons. For simplification we will assume that all methyl groups have the same relaxation time  $T_1$ .  $T_1$  of course is the \_\_\_\_\_ or \_\_\_\_\_ relaxation time. Give the pulse sequences for the inversion recovery experiment. Use the usual pulse diagrams and indicate precisely the types of the pulses. (2 point)

H-Channel:

(1 points)

C-Channel:

(4 points)

Using the rotating frame description of the NMR experiment, describe the C magnetization at the various times indicated. Label all axes. (3.5 points each part = 14)

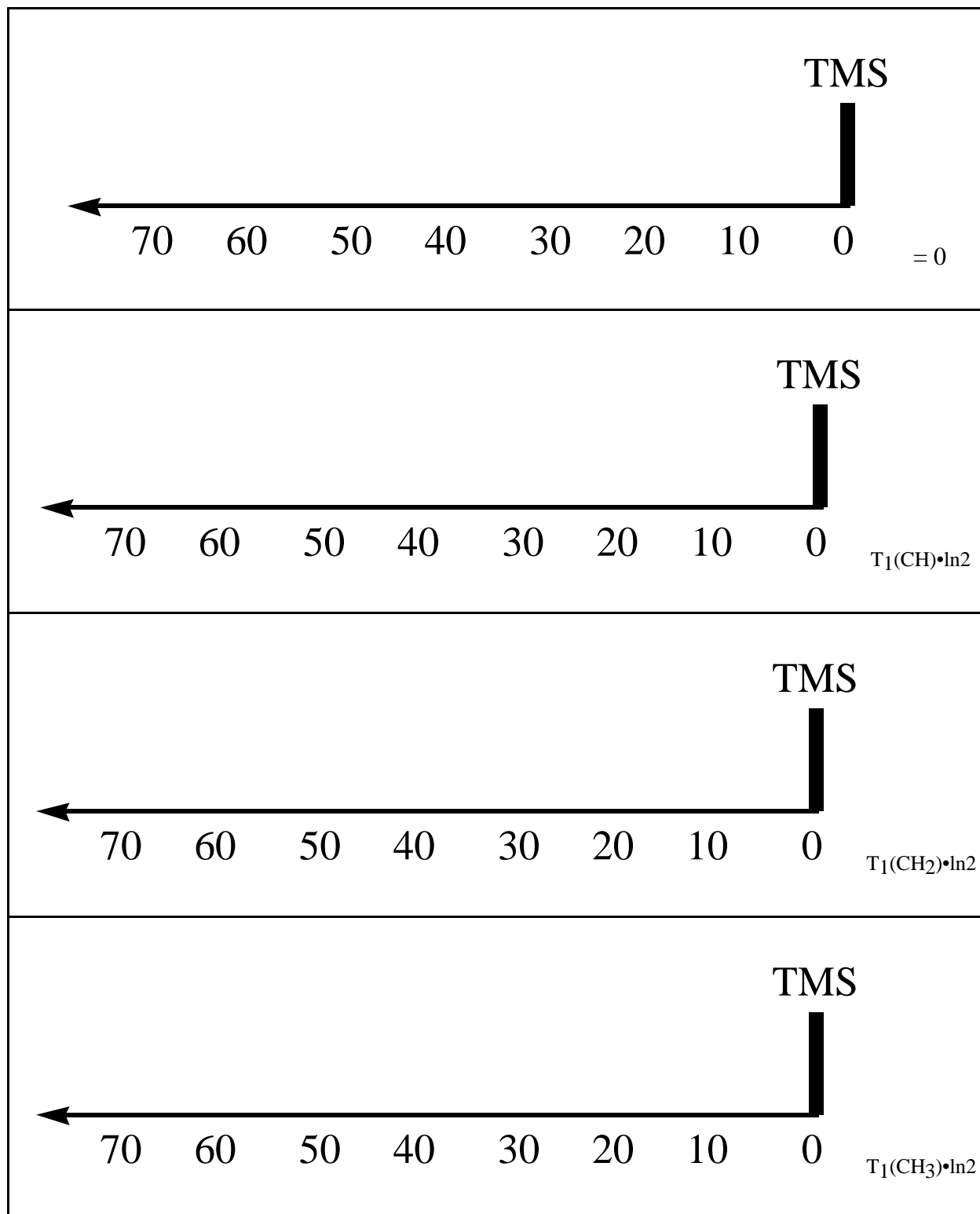
at the beginning of the experiment

after the  $180^\circ$  pulse

before the  $90^\circ$  pulse using  $\tau < T_1 \ln 2$

before the  $90^\circ$  pulse using  $\tau > T_1 \ln 2$

(b) There are three types of C atoms in the ether. Remember that we assume that all the methyl groups have the same relaxation time  $T_1$ . Draw the three spectra that are obtained after delay times that equal  $= 0$ ,  $T_1(\text{CH}) \cdot \ln 2$ ,  $T_1(\text{CH}_2) \cdot \ln 2$ , and  $T_1(\text{CH}_3) \cdot \ln 2$ . (3 points each) = 12)



**Question 5. 1-Dimensional Multiple-Pulse Experiments**

The idea here is simply that we produce spectra that allow for an easy distinction of the various types of C atoms without having the drawbacks associated with line overlap due to coupling. So, we are getting the coupling information not through the multiplicity but through some other type of information.

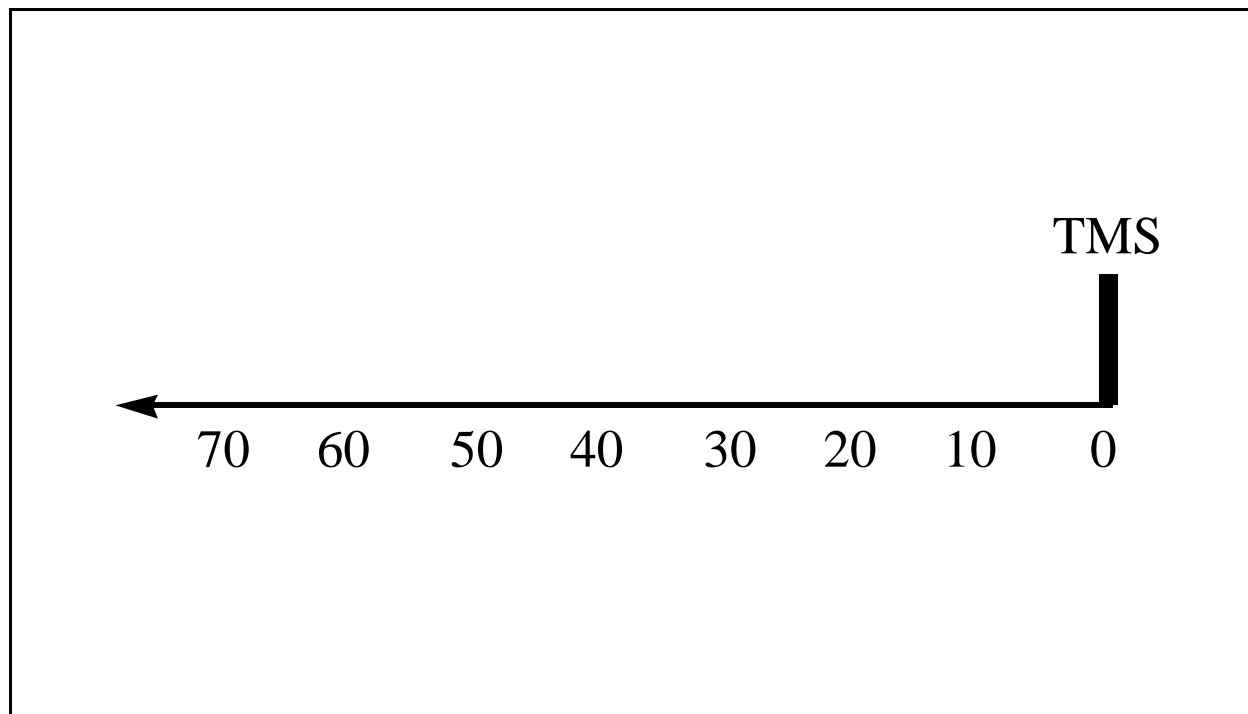
**(a) The J-Modulated Spin Echo Experiment.**

Give the pulse sequences for this experiment. Use the usual pulse diagrams and indicate precisely the types of the pulses. (2 and 2 points = 4)

H-Channel:

C-Channel:

Draw the J-modulated spin echo spectrum for the ether. (4 points)



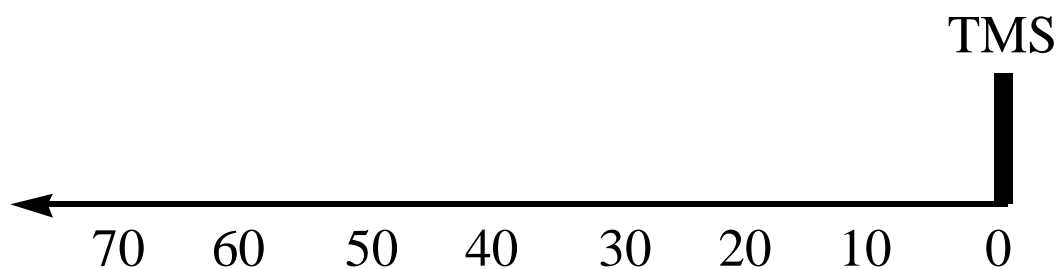
(b) The SPI Experiment.

SPI stands for \_\_\_\_\_ . (1 point)

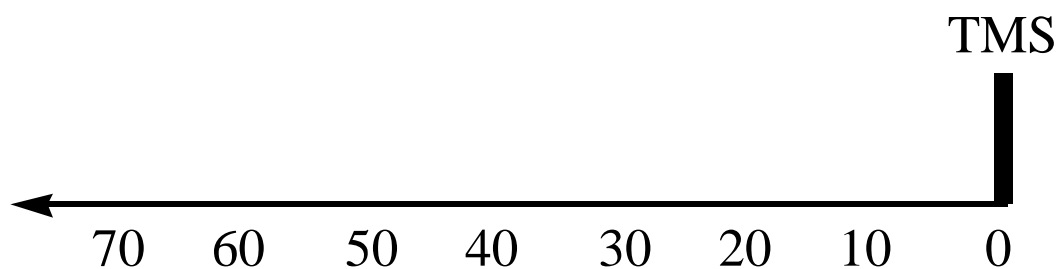
As the name says, this is an experiment in which we can increase some C signals by manipulation of the states of the H atoms. Moreover the experiment is selective; so we can modify just one atom at a time. Note that the BB decoupler is not on! So the C spectrum does show splitting due to  $^1J(C,H)$ .

Draw the  $^{13}C$  NMR SPI spectra obtained upon application of a selective 180 degree pulse to the  $^1H$  signal indicated. (4 points each = 8)

Irradiate the  $^{13}C$  satellite at the high chemical shift side of the CH  $^1H$ -signal:



Irradiate the  $^{13}C$  satellite at the low chemical shift side of the CH  $^1H$ -signal:

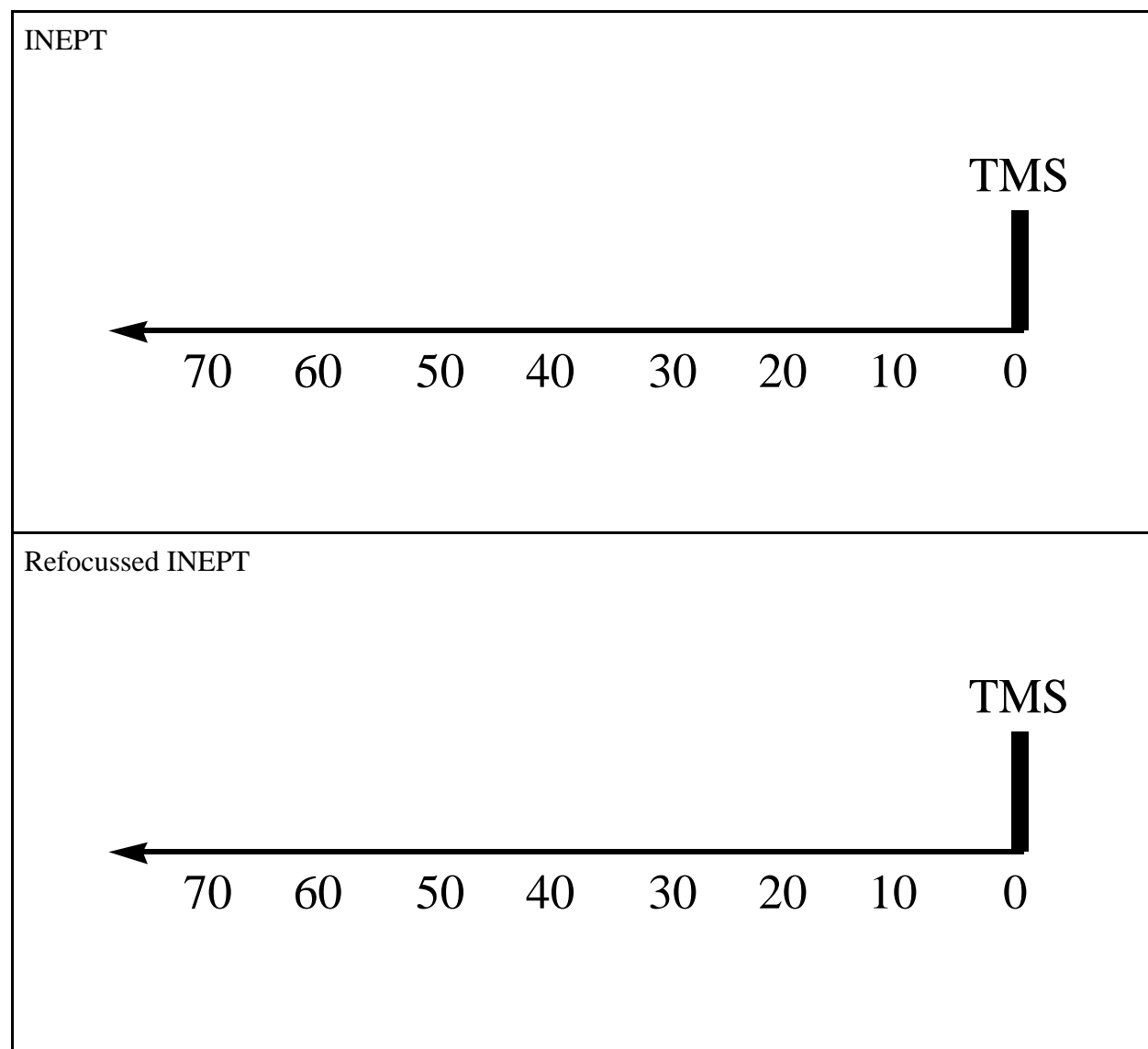


(c) INEPT experiments.

INEPT stands for \_\_\_\_\_.

The advantage of this experiment is that it basically gives the same information as the SPI experiment but for all types of C atoms at the same time. How nice. A variation of the INEPT experiment is the *refocussed INEPT* experiment. The advantage of the latter is that the multiplets remain. For example, a regular triplet shows up in the INEPT as \_\_\_\_\_ lines while it shows up in the refocussed INEPT as \_\_\_\_\_ lines. Draw the INEPT and the refocussed INEPT spectra of the ether. Pay attention to the line intensities (get them qualitatively correct)!

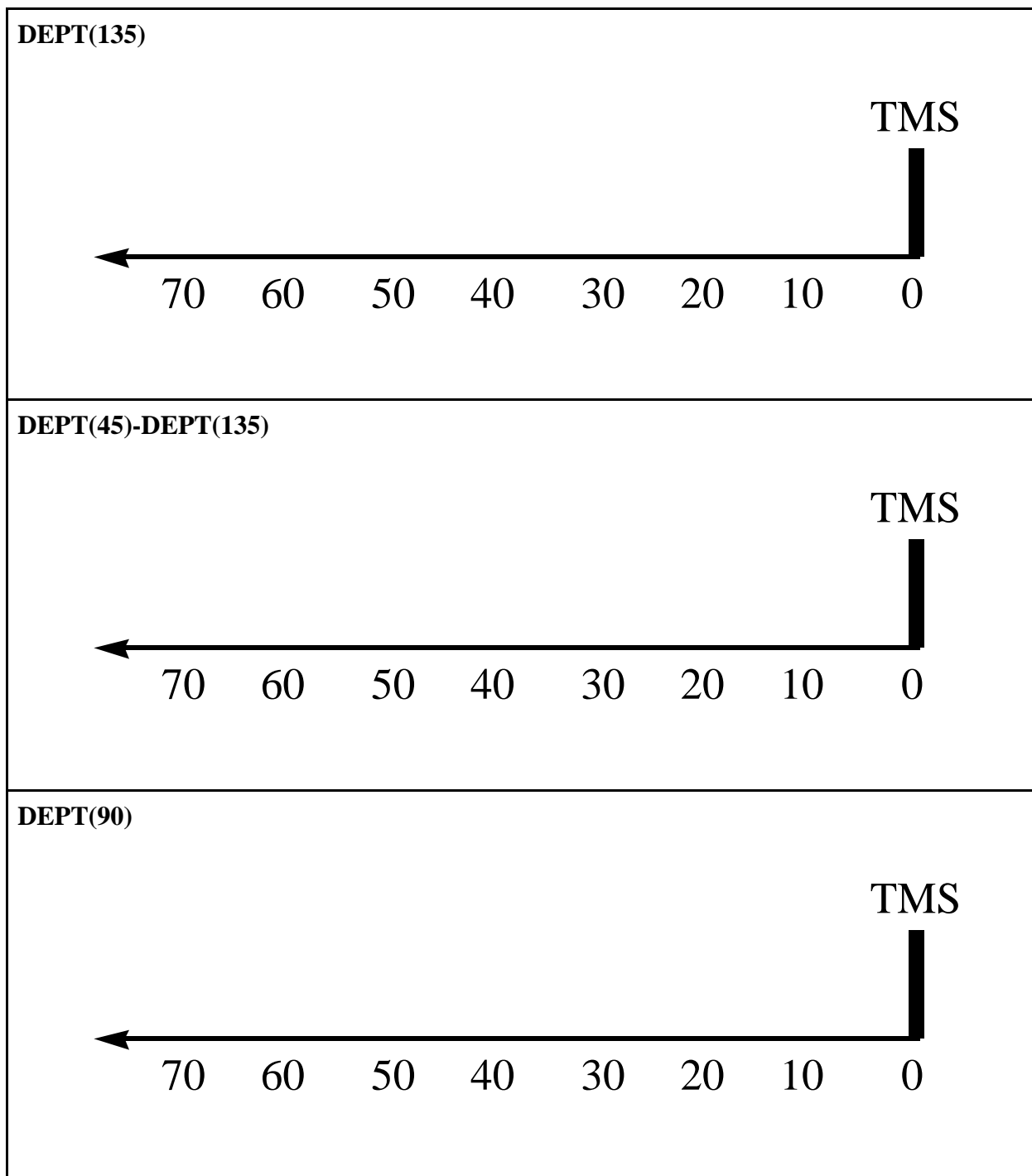
(1 point each blank, 4 each spectrum = 11)



(d) DEPT Experiment.

DEPT stands for \_\_\_\_\_.

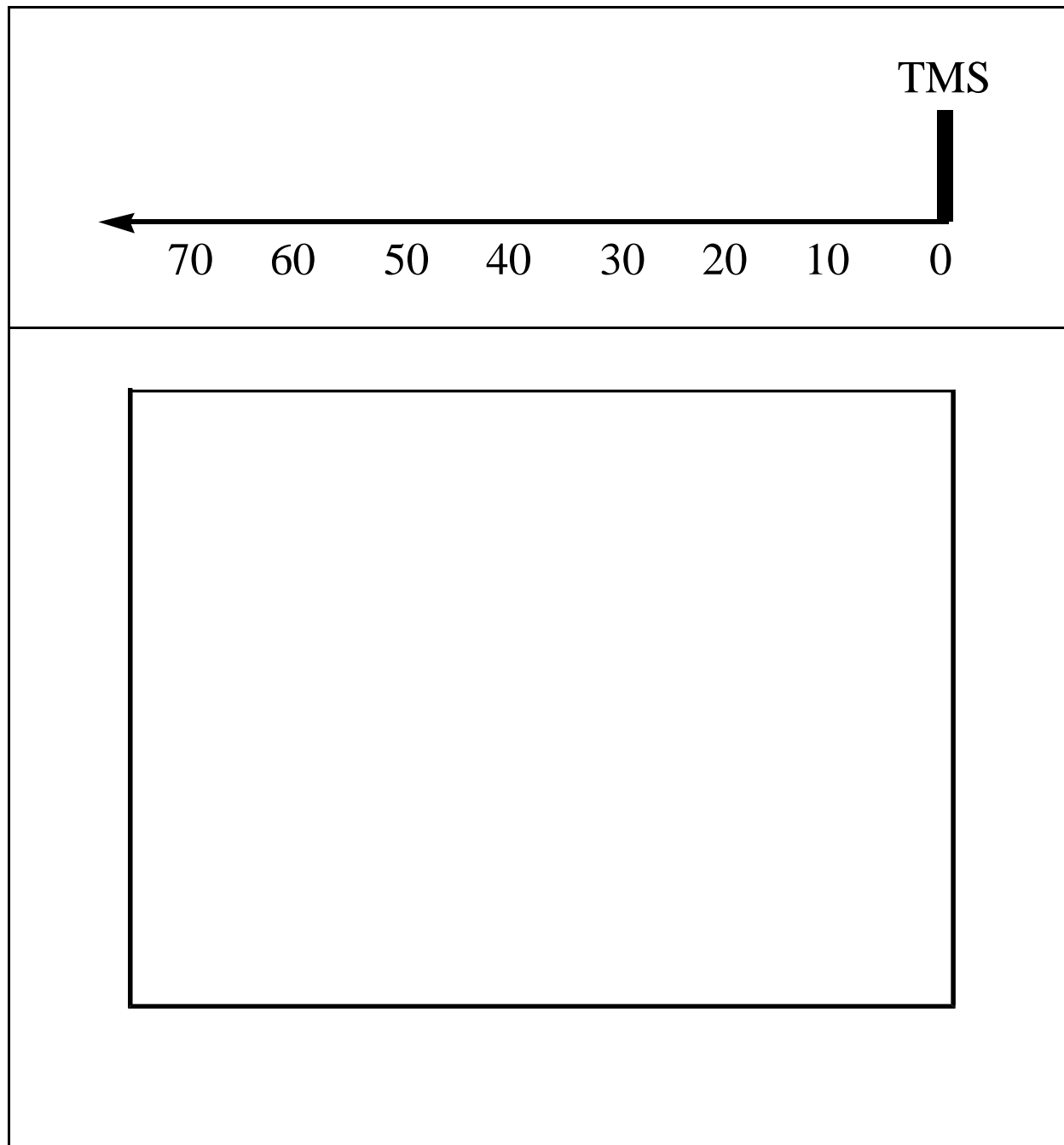
Draw the three spectra and indicate for each what types of  $\text{CH}_x$  C signals do show up positive or negative. (1 for the blank, 3 each spectrum = 10)



**Question 8.** 2-Dimensional Experiments. (10 points each part = 30)

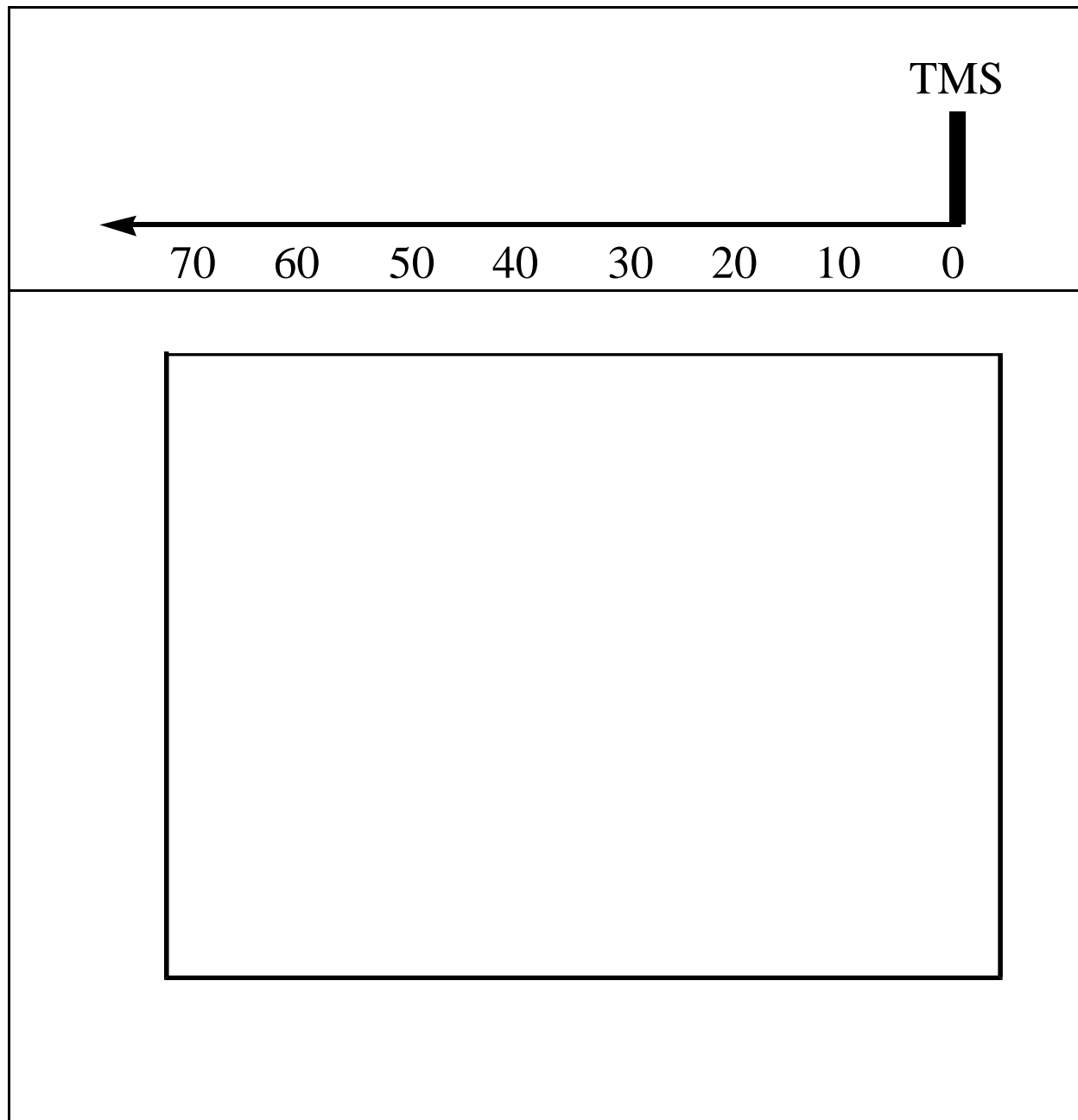
(a) Heteronuclear Two-Dimensional J-Resolved  $^{13}\text{C}$  NMR spectroscopy.

Draw the contour diagram obtained from this experiment for the ether. Do these things: (a) Draw the C-spectrum on top (pay attention whether it is or is not coupled). (b) Label the axes of the 2-D plot. Give numbers and units. (c) Draw the contour plot.



(b) Two-Dimensional H,C-correlated NMR - (H,C) COSY

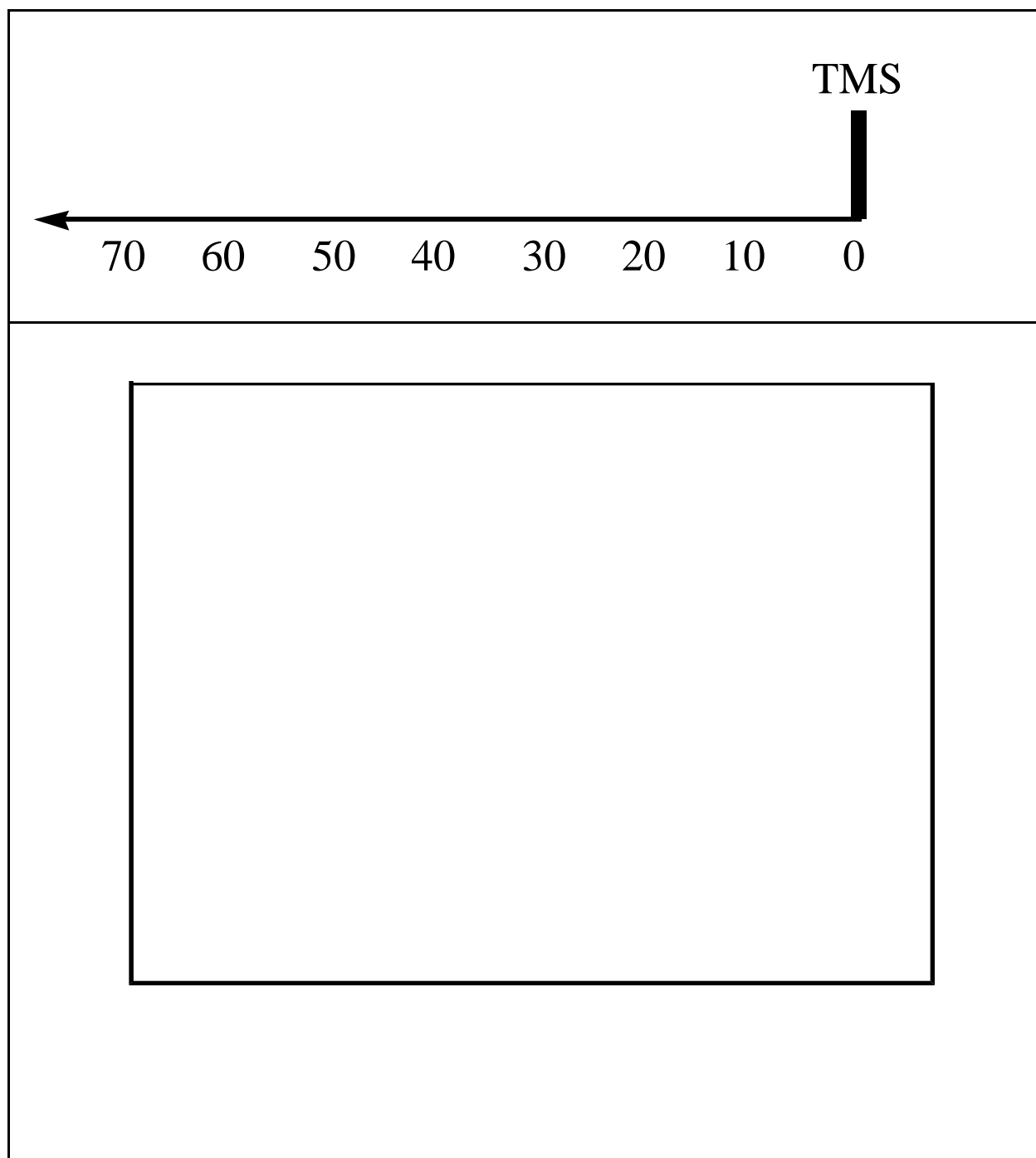
Draw the contour diagram obtained from this experiment for the ether. Do these things: (a) Draw the C-spectrum on top (pay attention whether it is or is not coupled) and draw the H spectrum on one of the sides. (b) Label the axes of the 2-D plot. Give numbers and units. (c) Draw the contour plot. (d) Indicate with horizontal and vertical lines what H-signals are correlated with the C(2) signal.





(c) Two-Dimensional H,H-correlated NMR - (H,H) COSY

Draw the contour diagram obtained from this experiment for the ether. Do these things: (a) Draw the H-spectrum on top and on left sides. (b) Label the axes of the 2-D plot. Give numbers and units. (c) Draw the contour plot. (d) Indicate with squares what other H-atoms the H(3) atoms are correlated to.



The Final will be graded on Tuesday afternoon and Wednesday morning. You can look at your Final after I posted the results outside my office. You can inquire about your final grade on Thursday. You may also pick up your paper after Thursday.

Enjoy your vacation. Relax in a longitudinal fashion with  $T_1 = 1$  week!

