Practice Exam 3

Chemistry 605 (Reich)

THIRD HOUR EXAM

Mon. May 10, 2010

Question/Points	
R-09N	/20
R-09O	/15
R-09P	/15
R-09Q	/15
R-08R	/25
R-08S	/10
Total	/100

Name_____

If you place answers anywhere else except in the spaces provided, (e.g. on the spectra or on extra pages) clearly indicate this on the answer sheets.

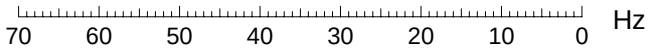
Problem R-09N (C_5H_9DO) Yes, that's a deuterium. Determine the structure from the 200 MHz ^1H NMR spectrum.

(a) DBE_____ (b) Interpret the multiplets at δ 4.95 and δ 5.95. Report coupling in the standard format ($^nJ_{x-y}$ = 00 Hz). Show part structure(s) suggested by these peaks

δ 4.95

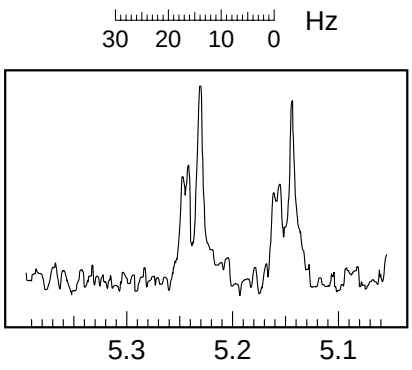
δ 5.95

(c) On the Hz scale below sketch what the proton at δ 5.95 would look like in the undeuterated compound ($C_5H_{10}O$)



(d) Draw the structure of R-09N. If more than one structure is possible, then draw them, but circle the one you prefer.

(e) The boxed inset between δ 5.1 and 5.3 (reproduced below) is an 8x vertical expansion. Suggest what these small impurities might be due to, and assign the peaks..

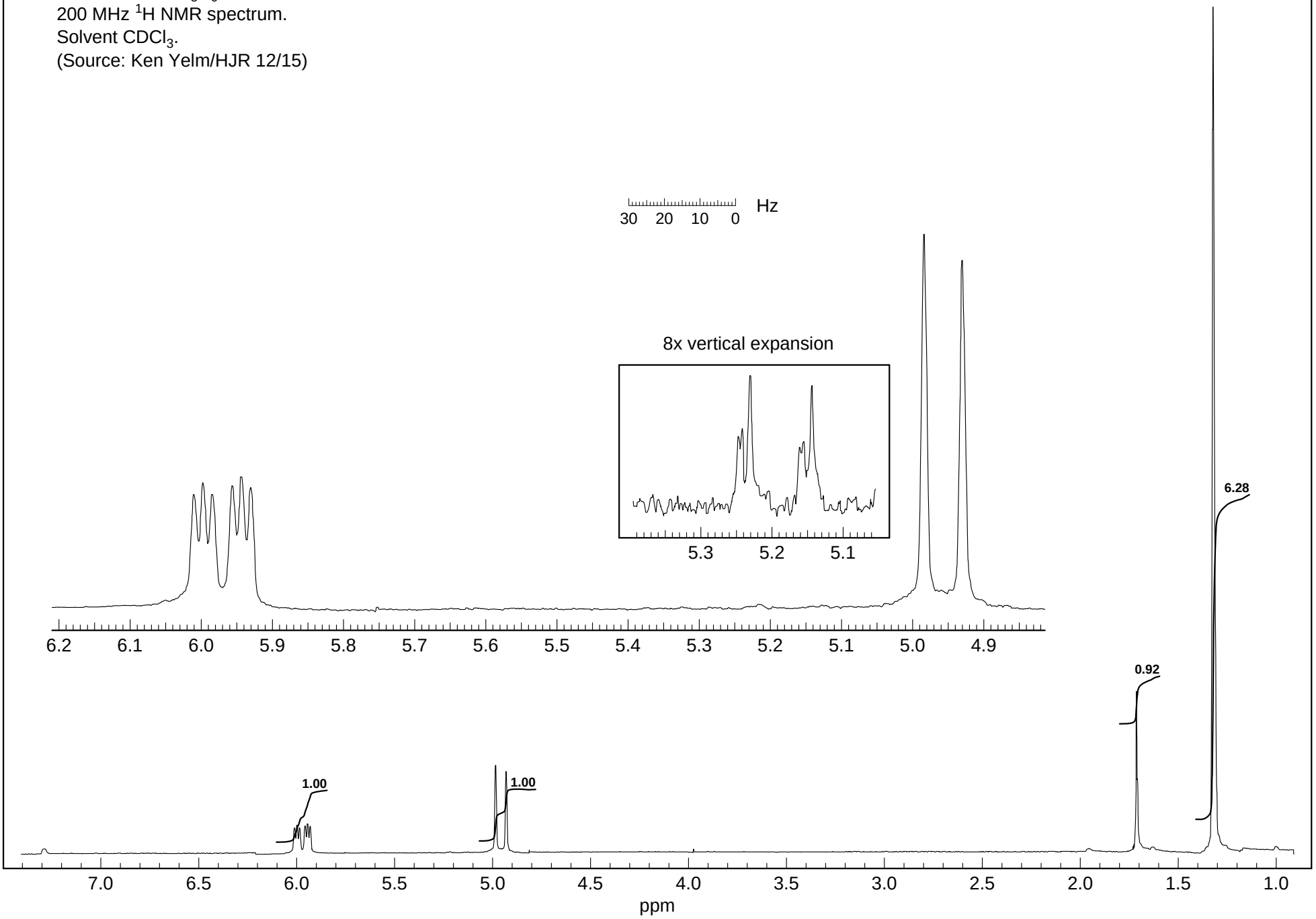


Problem R-09N C_5H_9DO

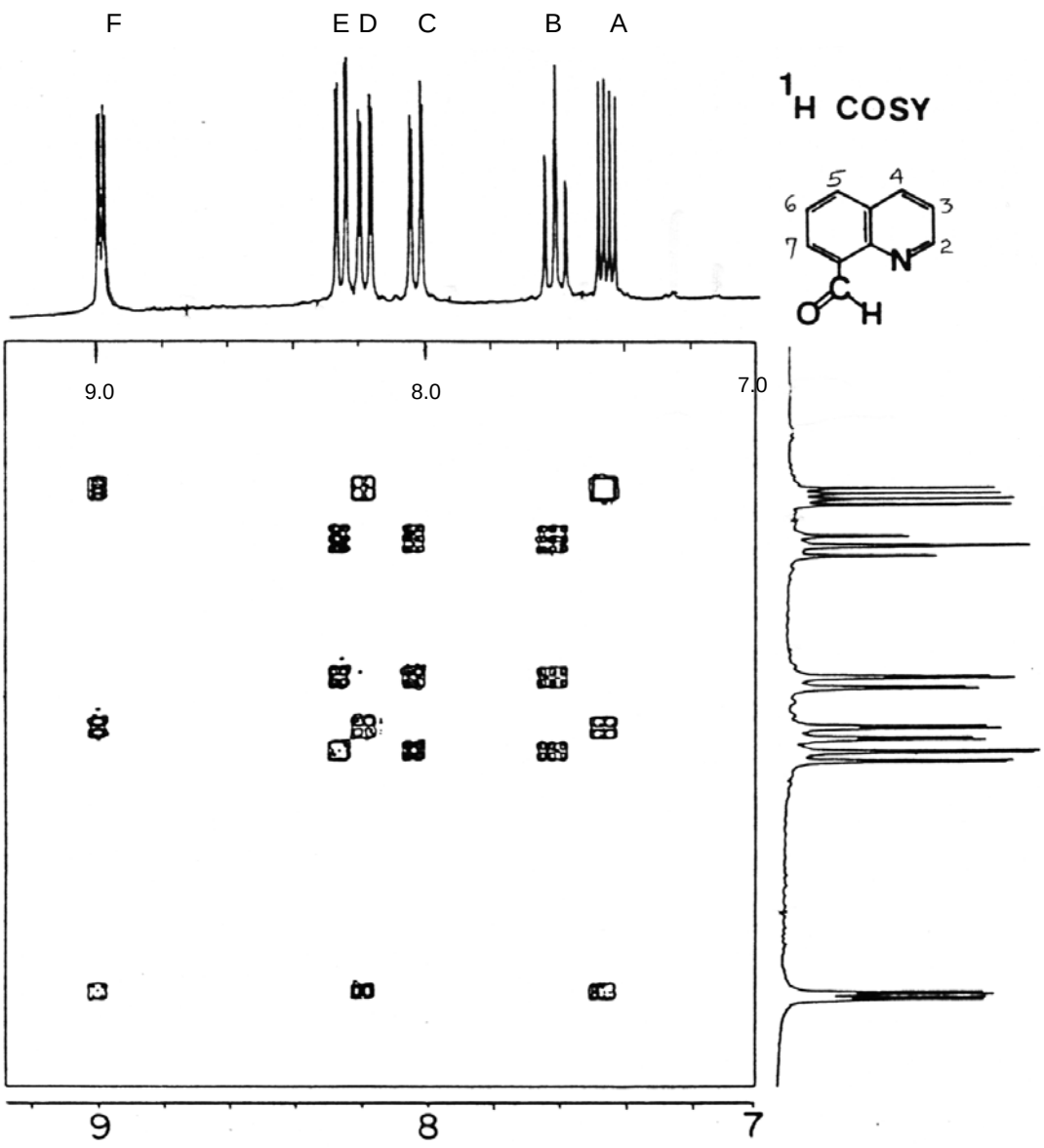
200 MHz ^1H NMR spectrum.

Solvent $CDCl_3$.

(Source: Ken Yelm/HJR 12/15)



Problem R-09O ($C_{10}H_7NO$). Shown below is the 250 MHz proton homonucear shift correlated spectrum (H,H-COSY) of quinoline 8-carboxaldehyde. The aldehyde proton at δ 9.5 is not shown.



Asign the proton signals A through F to the protons H^2 to H^7.

H^2 = _____

H^3 = _____

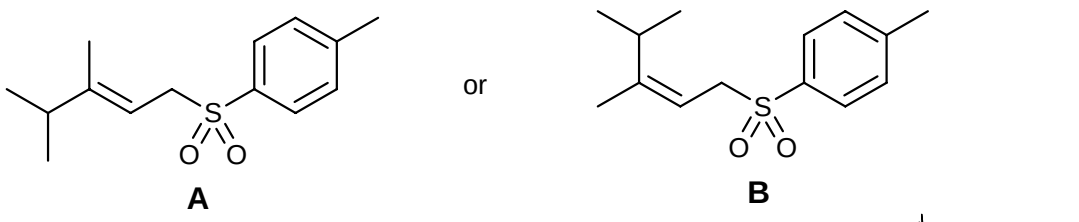
H^4 = _____

H^5 = _____

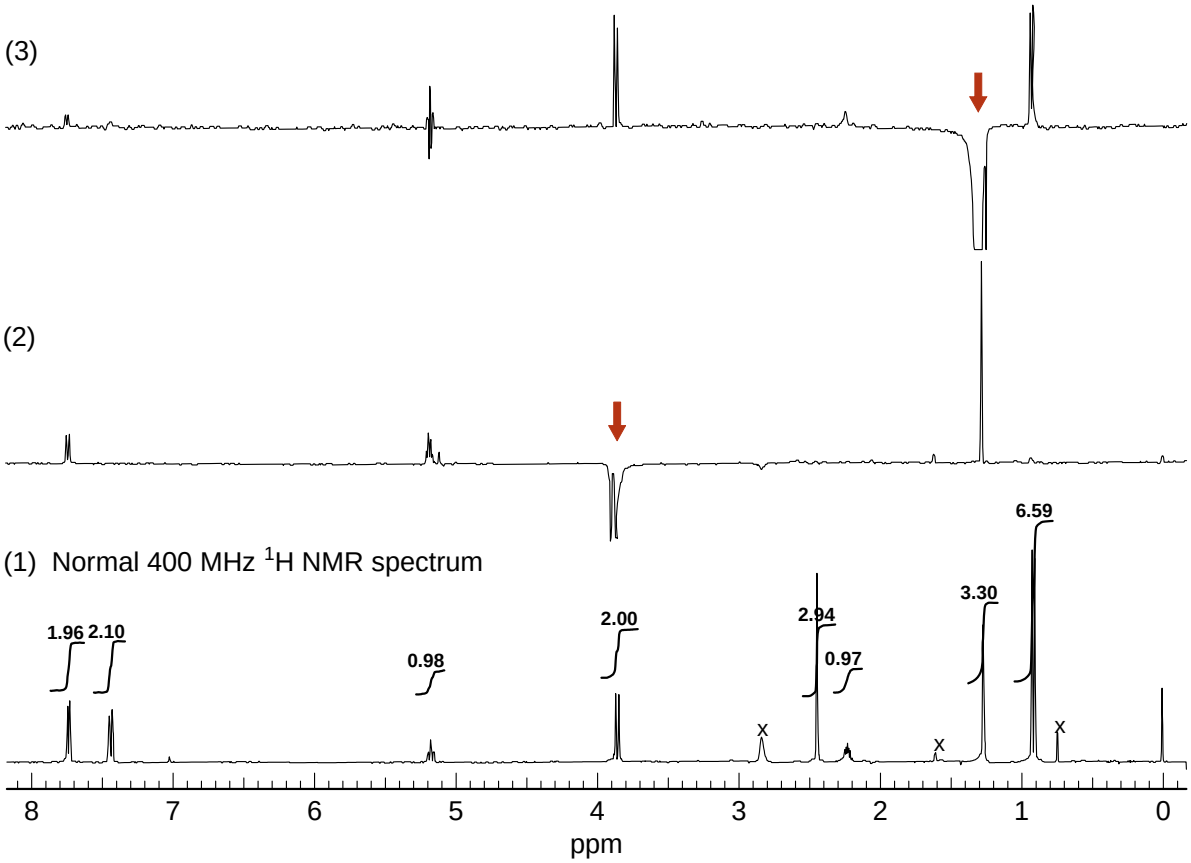
H^6 = _____

H^7 = _____

Problem R-09P ($C_{14}H_{20}O_2S$). Spectrum (1) is a normal 400 MHz ^{1}H NMR spectrum of one of the isomers shown. Impurity peaks are marked with x. Spectra (2) and (3) are difference spectra, in which the normal spectrum is subtracted from the spectrum obtained by preirradiating for a few seconds at the frequency shown by the arrow



A **B**

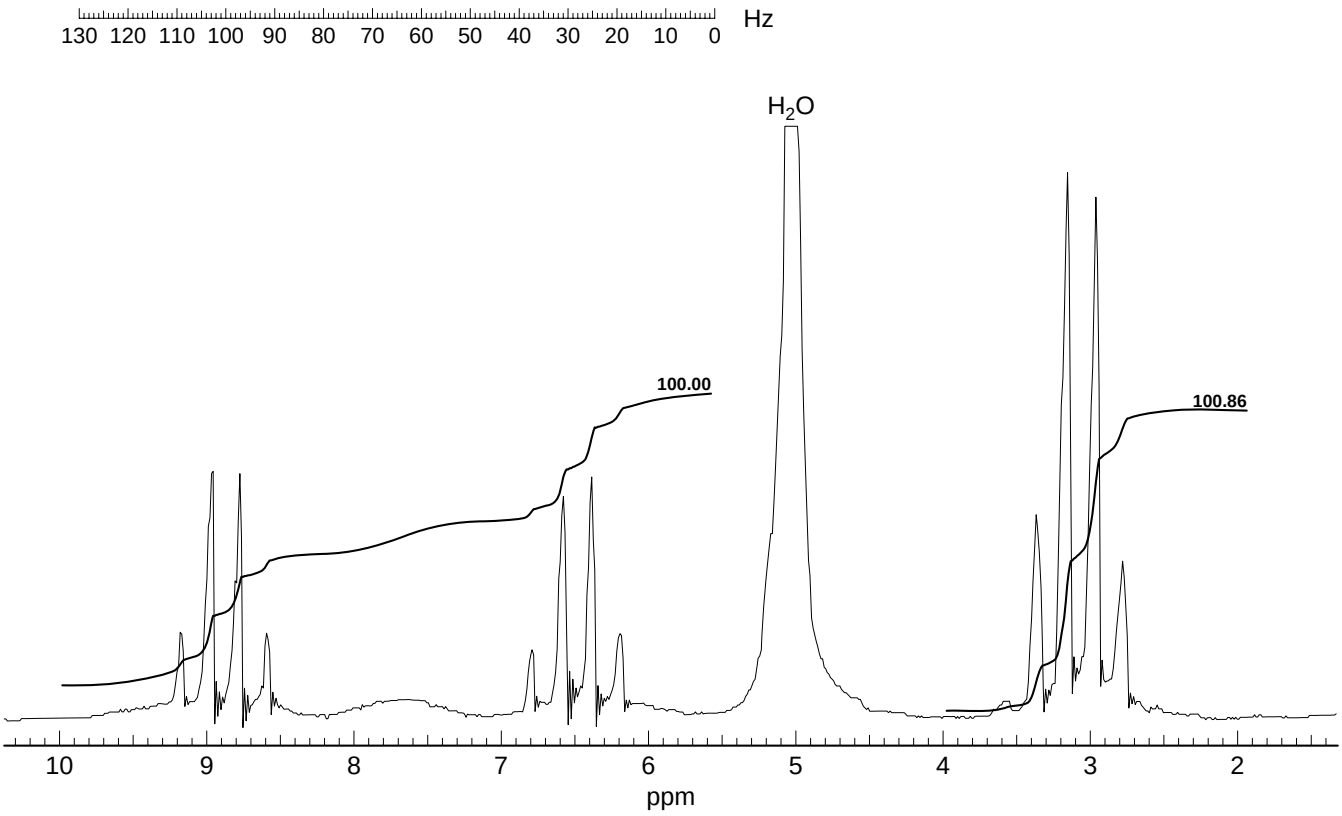


(a) What kind of experiment is being done here?

(b) Which of the isomers is the correct structure (**A** or **B**)?_____ Explain briefly, but be specific.

(c) Assign the protons by writing chemical shifts on the correct structure.

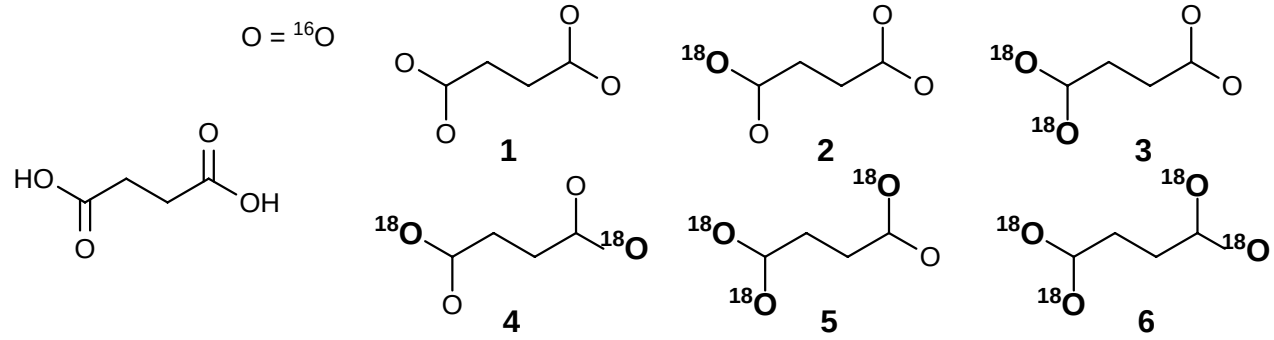
Problem R-09Q (C_1H_6ClN). Shown below is the 30 MHz ^1H NMR spectrum of 60% ^{15}N enriched $CH_3NH_3^+$ Cl^- in H_2O



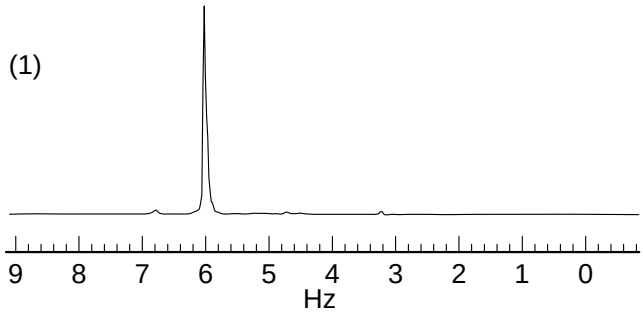
Identify all significant peaks by labelling the spectrum. Show all coupling constants in the standard format $^nJ_{x\text{-}y}$ = 00 Hz.

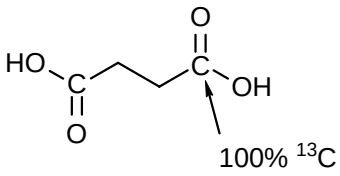
Problem R-09R. Interpret the proton noise decoupled 50.3 MHz ^{13}C NMR spectra of ^{13}C and ^{18}O labelled succinic acid. Only the carbonyl region is shown - the signals appear at δ 176.

There are 6 possible different ^{18}O labelled succinic acids (isotopomers), drawn as compounds 1-6 below. Under the conditions of the NMR experiment, proton/deuterium transfers are fast, so the protons/deuterons are not shown.



Spectrum (1) shows mono-^{13}C labelled succinic acid with ^{18}O at natural abundance (0.2%) (compound **1**).





(a) Interpret spectrum (2) reproduced below. This sample was produced by heating a sample of succinic acid in $H_2{}^{18}O$ (ca 52% ^{18}O incorporation) and contains all 6 isotopomers (**1**-**6**). Show you understand the origin of the three peaks by sketching the signals you would expect to see for a sample of each pure isotopomer **2** to **6**.

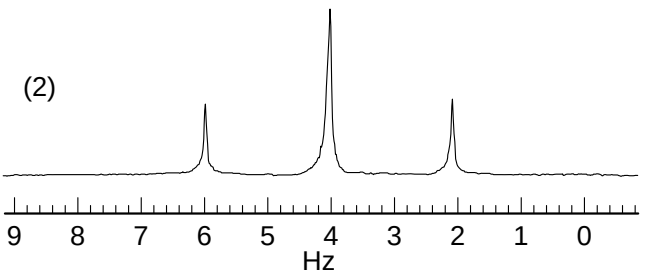
Pure **6**

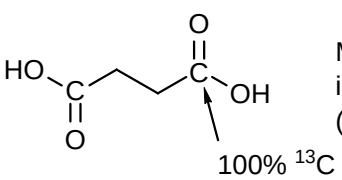
Pure **5**

Pure **4**

Pure **3**

Pure **2**



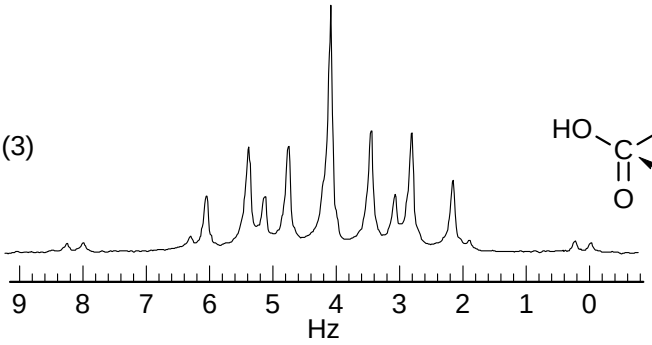


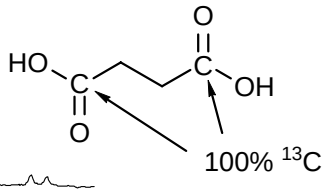
Mono-^{13}C labelled, after heating in $H_2{}^{18}O$ for some time (mixture of isotopomers **1** to **6**)

(b) The sample for spectrum (3) was prepared similarly to spectrum (2), except that succinic acid was used in which both carboxyl groups are labelled 100% with ^{13}C. To help you get started in your analysis, sketch the spectrum you would expect for a pure sample of isotopomer **2**.

Pure **2**

(3)

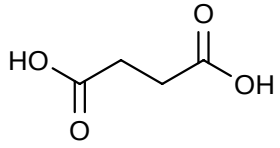


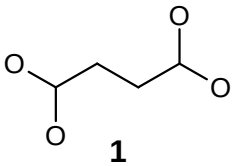


Double ^{13}C labelled,
after heating in $H_2{}^{18}O$ for some time
(mixture of isotopomers **1** to **6**)

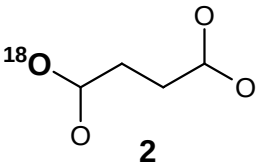
(c) On spectrum (3), mark the peaks which correspond to isotopomers **1**, **2**, **3**, **4**, **5** and **6** by placing numbers on the appropriate peaks (amazingly, there are no superimposed peaks!). Make sure you account for the small peaks (i.e., those at 0.0, 0.3, 2.0, 6.3, 8.0 and 8.3 Hz). Report and identify any coupling constants you can measure.

Here is all the data in one place:

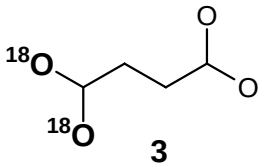




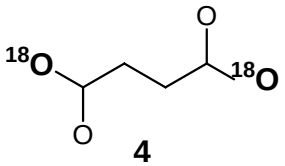
1



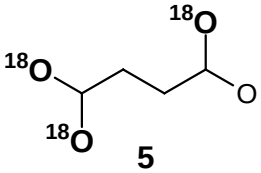
2



3



4



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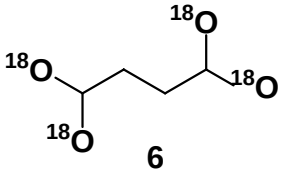
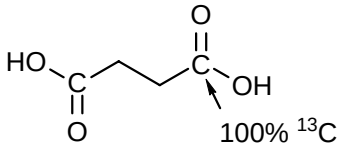


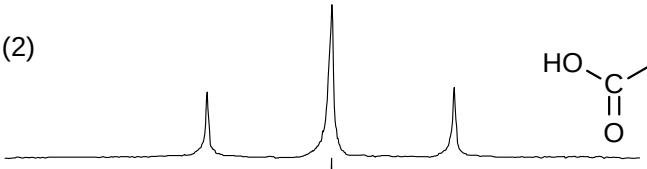
6

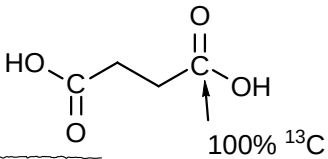
(1)



Mono-^{13}C labelled, with ^{18}O at natural abundance (0.2%) (compound **1**).

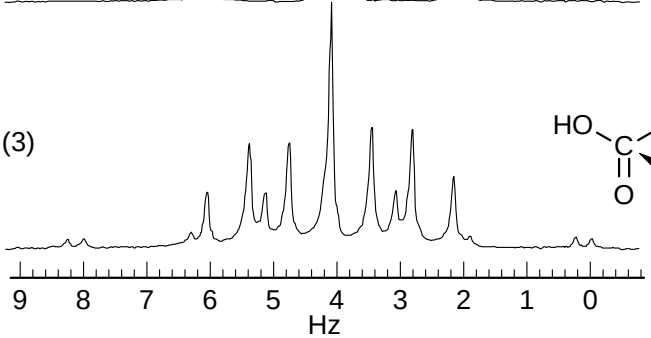
(2)

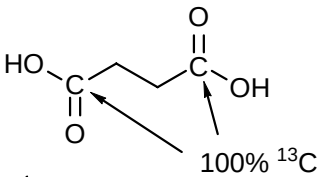




Mono-^{13}C labelled, after heating in $H_2{}^{18}O$ for some time (mixture of isotopomers **1** to **6**)

(3)



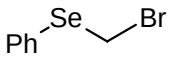


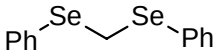
Double ^{13}C labelled,
after heating in $H_2{}^{18}O$ for some time
(mixture of isotopomers **1** to **6**)

Problem R-09S. The 200 MHz ^{1}H NMR spectrum of a mixture of two selenides (approx a 2:1 ratio) is shown below. The compounds are bis(phenylseleno)methane and bromo(phenylseleno)methane.

(a) Identify all of the peaks in the region δ 4 to δ 5. Give chemical shifts and any couplings you have identified.

Mixture:





(b) Identify **<u>two</u>** distinct features of the spectrum which allow you to unambiguously assign which signal corresponds to which compound.

Method 1:

Method 2:

Problem R-09S $C_{13}H_{12}Se_2$

200 MHz ^1H NMR spectrum.

Solvent $CDCl_3$.

(Source: R. D. Dykstra/Reich 12/26)