

CHM 4380
Final Examination

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Name: _____

Student number: _____

Time allowed: 3 hours

Basic non-alphanumeric calculator permitted

This exam has 6 pages.

Instructions: Circle the single most appropriate response for each of the 25 questions. All questions are valued equally.

1. A nucleus having spin quantum number, $I = 1$:
 - a) will have 1 energy transition but only when in an external magnetic field.
 - b) has 3 Zeeman energy levels in the absence of an external magnetic field.
 - c) has spin quantum numbers, $m = \frac{1}{2}, 0, -\frac{1}{2}$.
 - d) is quadrupolar**
 - e) is not NMR active.

2. A NOESY pulse sequence:
 - a) is a 2D experiment used to measure J coupling correlations between two unlike isotopes.
 - b) uses pulsed field gradients to distinguish between molecules with different diffusion constants.
 - c) can show correlations between protons close to one another in space and also between protons exchanging with one another.**
 - d) is one of the simplest imaging sequences.
 - e) requires a triple resonance NMR probe.

3. A variable evolution delay:
 - a) is used when all resonances have very long T_1 relaxation times.
 - b) must always be used between short high power $(\sin x)/x$ pulses.
 - c) is used in all 2D pulse sequences.**
 - d) is less important for running liquids NMR rather than solids NMR.
 - e) is used to get around the receiver dead time problem.

4. The J modulated spin echo experiment:
- is used to measure $^1\text{H} - ^1\text{H}$ coupling constants.
 - uses a fixed delay equal to $1/(J_{\text{C-H}})$ to phase encode ^{13}C resonances based on the number of attached protons.
 - is most often run as a 2D experiment except Fourier transformations in the indirect domain are not calculated.
 - requires the use of the proton decoupler for the entire duration of the pulse sequence.
 - is used to make relaxation time measurements for J coupled spins.
5. A technique which can significantly improve rolling baseline problems in a spectrum is:
- backward linear prediction.
 - exponential line broadening.
 - resolution enhancement by using a Gaussian weighting function on the FID.
 - zero filling
 - quadrature detection.
6. The splitting in a ^1H NMR spectrum between the 3 lines of a J coupled triplet is 12 Hz when measured on a 300 MHz spectrometer. The splitting:
- would be 24 Hz if measured on a 600 MHz spectrometer.
 - would be 0.04 ppm if measured on a 600 MHz spectrometer.
 - would be 0.02 ppm if measured on a 600 MHz spectrometer.
 - would be 0.08 ppm if measured on a 600 MHz spectrometer.
 - would not be equal to any of the above on a 600 MHz spectrometer.
7. The signal-to-noise ratio in an NMR spectrum was much lower than expected. What was the problem?
- The relaxation delay was too long.
 - The pulse used was much less than 90° .
 - There was a problem with the zero filling.
 - The excitation profile of the pulse was too wide.
 - The resources of the computer running the spectrometer were being shared by a web browser.
8. All of the lines in a particular NMR spectrum have a distortion which broadens the lines symmetrically at the base. What would explain the problem?
- There was a significant receiver dead time after the pulse.
 - The Z^2 and Z^4 shims were set poorly.
 - The Z^3 and Z^5 shims were set poorly.
 - The excitation profile of the pulse was too narrow.
 - The acquisition time was not long enough.

9. The literature value for the ^{29}Si chemical shift of tetramethylsilane (TMS) is 0.00 ppm. A proton decoupled ^{29}Si NMR spectrum of TMS was acquired without the use of digital filters. The carrier frequency was set at -50 ppm and the spectral width set at 90 ppm. Which statement best describes the spectrum?

- a) A signal at 0.00 ppm.
- b) No signal.
- c) A signal at -55 ppm.
- d) A signal at -180 ppm.
- e) A signal at -90 ppm.

10. The inversion transfer experiment can be used to:

- a) measure T_2^* .
- b) measure T_1 .
- c) distinguish between the components of a mixture based on their diffusion coefficients.
- d) detect chemical exchange.
- e) help determine how many protons are attached to a carbon.

11. How many lines are in the ^{19}F NMR spectrum of the isotopomer $^{13}\text{CDF}_3$? (The spin quantum numbers for ^2H , ^{19}F and ^{13}C are $I = 1$, $I = \frac{1}{2}$ and $I = \frac{1}{2}$, respectively.)

- a) 6
- b) 16
- c) 4
- d) 3
- e) 2

12. A ^1H NMR spectrum of H_2^{77}Se consists of a 1:1 doublet. The $^1J_{\text{Se-H}}$ coupling constant is 64.8 Hz. The plot has the peaks labelled in ppm as -0.1843 and -0.3139 ppm. Which spectrometer was used to run the spectrum?

- a) Nicolet 360
- b) Varian XL-300
- c) Bruker AVANCE 400
- d) JEOL ECLIPSE 930
- e) Bruker ARX 500

13. The rotating frame of reference:

- a) is a mathematical concept used to help explain why some gyromagnetic ratios are negative.
- b) always rotates at the proton Larmor frequency.
- c) is a concept which helps simplify the description of magnetization vectors in the presence of a magnetic field under the influence of radio frequency pulses.
- d) is a mathematical concept where the YZ plane of a Cartesian axis system rotates about the X axis.
- e) is not described accurately by any of the above.

14. The free induction decay:

- a) follows the decay of magnetization on the z axis.
- b) is a frequency domain function.
- c) always decays according to the T_1 relaxation time constant.
- d) can change its appearance depending on the position of the carrier frequency.
- e) all of the above are true.

15. Superconducting magnets require an external source of power:

- a) to slow down the evaporation of liquid helium.
- b) to cool the solenoid coil of the magnet to 77 K.
- c) to keep the magnet shims cold so they will not generate noise.
- d) to keep the NMR probe cool.
- e) only when being brought up to their specified field strength.

16. A technique which can be used to eliminate Nyquist fold-backs and increase the signal-to-noise ratio in an NMR spectrum is:

- a) digital filtering.
- b) backward linear prediction.
- c) forward linear prediction.
- d) apodization of the FID with a Gaussian function.
- e) zero filling.

17. The following pulse sequence:

$(90_{-y}) - (180_x) - (90_y) - (180_x)$

would leave an equilibrium magnetization along the:

- a) x axis.
- b) y axis.
- c) -z axis.
- d) -x axis.
- e) -y axis.

18. Exponential line broadening:
- a) is a processing technique used to improve digital spectral resolution.
 - b) has the effect of artificially expanding the spectra width.
 - c) can be used to recover information lost in the spectrometer dead time.
 - d) can improve the signal-to-noise ratio in a spectrum at the expense of resolution.
 - e) eliminates Nyquist fold-backs.
19. A properly recorded NMR spectrum acquired with 16 scans had a signal-to-noise ratio of 2. How many scans would be needed to get a signal to noise ratio of 20?
- a) 160
 - b) 320
 - c) 1,600
 - d) 3,200
 - e) 16,000
20. The spectrometer amplifier power:
- a) affects the spectral width.
 - b) is an important parameter to ensure that the receiver dead time is kept to a minimum.
 - c) can affect the resolution in an NMR spectrum.
 - d) affects T_2^* but not T_1 or T_2 .
 - e) affects the duration of 90° pulses.
21. The observed line width at half height of an NMR signal, $\Delta\nu_{1/2}$, for a liquid:
- a) depends on the relaxation delay allowed in the pulse program.
 - b) tends to be larger for nuclei with larger gyromagnetic ratios.
 - c) is inversely proportional to T_1 .
 - d) depends on T_2^* .
 - e) depends critically on the receiver dead time.
22. Solenoid r.f. coils are generally not used in NMR probes designed to collect NMR data for liquid samples because:
- a) they make sample handling cumbersome.
 - b) they are less efficient at transmitting r.f. power to the sample than Helmholtz coils.
 - c) they are not superconducting.
 - d) they are much more expensive to incorporate into an NMR probe.
 - e) they make an NMR probe difficult to tune and match.

23. 1-Dimensional TOCSY NMR data:

- a) requires the use of a variable delay.
- b) requires the use of a shaped pulse.
- c) can be used to determine whether nuclei are quadrupolar.
- d) can be used to determine whether or not two protons are close to one another in space.
- e) is described accurately by all of the above.

24. Gated proton decoupling:

- a) would be used in conjunction with long recycle delays to acquire a quantitative ^{13}C NMR spectrum.
- b) would be used to observe a fully coupled ^{13}C spectrum with a nuclear Overhauser enhancement.
- c) can be used to determine T_1 .
- d) is a simple alternative to the COSY experiment.
- e) can only be applied during the dwell time between sampling points of the FID.

25. The intermediate frequency of an NMR spectrometer:

- a) is the frequency of the rotating frame of reference.
- b) is equal to the Larmor frequency.
- c) is the frequency difference between a resonance line and the center of the spectrum.
- d) is the intermediate frequency between that of ^1H and ^{13}C .
- e) is not described well by any of the above.