**CHUKA**  **UNIVERSITY**



# UNIVERSITY EXAMINATIONS

## EXAMINATION FOR THE AWARD OF DEGREE OF MASTERS OF SCIENCE IN CHEMISTRY

**CHEM 843: ADVANCED NMR TECHNIQUES**

**STREAMS: MSC (CHEM)** **TIME: 3 HOURS**

**DAY/DATE: TUESDAY 03/12/2019** **2.30 PM – 5.30 PM**

**INSTRUCTIONS:**

**ANSWER ALL QUESTIONS**

**QUESTION ONE (20 MARKS)**

(a) (i) Summarize the factors affecting the population differences between the lower energy state and the upper energy state and how is the population difference related to the NMR signal? [5 marks]

(ii) Recommend the most suitable probe for each of the following laboratories for NMR analysis.

(I) A laboratory involved in biochemical work or analytical studies on natural products. [1 ½ marks]

(II) A laboratory involved in the synthesis of phosphorus compounds and organometallic complexes. [1 mark]

(III) A laboratory where large scale synthesis of organic compounds carried out. [1 mark]

(IV) A laboratory where various nitrogenous bases are prepared and studied. [1 mark]

(iii) If the spectral width is inadequate to cover every peak in the spectrum, then some peaks in the downfield or upfield region may fold over and appear superimposed on the spectrum. Suggest how you can identify these folded signals. [3 marks]

(iv) A serious problem associated with quadrature detection is that we rely on the cancellation of unwanted components from two signals that have been detected through different parts of the hardware. This cancellation works properly only if the signals form the two channels are exactly equal and their phases differ from each other by exactly 90 since this is practically impossible with absolute efficiency, some so called "image peaks" occasionally appear in the center of the spectrum. Explain how you can differentiate between genuine signals and image peaks that arise as artifacts of quadrature detection. [1 mark]

(v) Discuss problems you would expect to encounter in the case of incorrect alignment of the pulse width during an NMR experiment. [3 marks]

(b) Explain why there is a need to process the data through two Fourier transformation operations whenever there is only one time variable during 2D experiment ie $t_1$ in NMR. [3 ½ marks]

**QUESTION TWO (20 MARKS)**

(a) (i) Explain to why there is more likely to have signals outside the spectral width (SW) in an average 2D NMR experiment than in a 1 D NMR experiment and also why do spectral widths in a 2D NMR need to be defined very carefully? And what effects will this have on the spectrum? [6 ½ marks]

(ii) What could be the possible reasons for noise in 2D NMR spectra and how can symmetrization be used to improve the quality and readability of the plot?

[ 4 ½ marks]

(iii) Why is degassing of sample solutions in NMR tubes essential before Nuclear over hauser effect (noe) experiments and why are aqueous solutions (solutions in not generally degassed in the NMR tubes? [3 marks]

(b) Discuss the various problems encountered when using solid state NMR in analysis. [6 marks]

**QUESTION THREE (20 MARKS)**

(a) (i) Explain how you can distinguish between C, CH, $CH_2$ and $CH_3$ carbons in the attached proton Test (APT) experiment. [2 marks]

(ii) In what respect is the Insensitive Nuclei Enhancement by Population Transfer (INEPT) experiment superior to the Attached Proton Test (APT) or Gated Spin-Echo (GASPE) experiments? [3 marks]

(iii) Describe the fundamental properties of an INEPT experiment. [3 marks]

(b) (i) What is transient Nuclear overhauser enhancement (nOe) and why it is considered to provide a better estimate of the internuclear distance (r) than the normal noe effect? [1 ½ marks]

(ii) Explain what is meant by three spin effects or indirect Nuclear Overhauser enhancement (noe) effect. When do such indirect effect matter? [5 ½ marks]

(iii) Explain briefly the dependence of the Nuclear overhauser Enhancement (noe) on molecular motion (tumbling) [3 ½ marks]

(iv) Give the advantages of the correlated spectroscopy (Cosy) experiment over the Cosy 90 experiment. [1 ½ marks]

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