

**Department of Chemistry** 

# Examination paper for KJ3021 – NMR

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**Examination time (from-to):** 

Permitted examination support material:

C: - approved calculator - ruler

Other information:

Language: English Number of pages: Number of pages enclosed:

> **Checked by:** Prof. Finn Aachmann

28/11-18

Date

Signature

#### Notes:

- In some of multiple choice questions more than one answer can be correct.
- *Circle letter(s)* before the correct answer(s)

#### Problem 1.

What is correct:

- a) Correlation signals in a NOESY spectrum are always positive
- b) NOE effect is suppressed by quadrupolar relaxation mechanism
- c) In presence of paramagnetic molecules, NOE is enhanced
- d) For medium size molecules (1-3 kDa) NOESY experiment is unreliable
- e) Increase of  $B_0$  field has no effect on NOE.

#### Problem 2.

(6 pts)

Match the experiments in the first column with the correct properties given in the first raw. See the example of <sup>13</sup>C BB experiment.

Spectrum property $\rightarrow$	Observed nucleus is		Signal enhancement by polarization	NOE signal enhancement	Always zero-order		
Experiment ↓	<sup>1</sup> H	<sup>13</sup> C	transfer		spectrum		
<sup>1</sup> H							
<sup>13</sup> C BB		X		Х	Х		
HSQC							
C,H-COSY/ HETCORR							
Reverse INEPT							
Gated decoupling 1D <sup>13</sup> C							
Inverse- gated decoupling							

(12 pts)

#### Problem 3.

Draw a scheme for the basic spin-echo pulse sequence and its effect on an AX spin system by using the vector model.

(10 pts)

#### Problem 4.

What happens with individual nuclear spins immediately after  $90^{0}_{x'}$  pulse?

	11	1 2	- 1
	<ul><li>a) They have phase coherence.</li><li>b) They are aligned along y-axis.</li><li>c) They start to precess with higher</li><li>d) They interchange the energy lev</li></ul>	r frequency. els.	(4 pts)
<b>Proble</b>	e <u>m 5.</u>		
Wh a) b) c) d) e) f) g) h)	hich of the following procedures is/ar use of a window function tuning and matching phase correction removal of magnetic field inhomoge pulse calibration FID acquisition spectrum calibration shimming	re considered as spectrun eneities	1 processing?
<u>Proble</u>	em 6. Suggest 2 methods for distinguishin	g enantiomers in NMR.	(9 pts)
1)			

2)\_\_\_\_\_

(8 pts)

### Problem 7.

1D and 2D NMR spectra of an unknown compound are shown on pages 4-7. Its molar mass is 249.12 gmol<sup>-1</sup>. Elucidate the structure and assign all <sup>1</sup>H and <sup>13</sup>C shifts.

(25 pts)

## <sup>1</sup>H spectrum















#### **HMBC** expansion



#### Problem 8.

A set of 1D and 2D NMR spectra shown on pages 8-21 belongs to one of structures A-D (page 8).

- a) To which of them?
- b) Assign all <sup>1</sup>H and a <sup>13</sup>C resonances of that compound. Write the shifts next to the according proton/carbon in the right structure.

(26 pts)

#### HMBC

### <sup>1</sup>H spectrum





#### <sup>1</sup>H spectrum – expansion

#### <sup>1</sup>H spectrum – expansions



#### <sup>13</sup>C spectrum and expansions





**DEPT-135 and expansions** 

HSQC











COSY



(wdd) g







(wdd) g





## **HMBC** expansion





#### Proton shifts for common organic compounds





1тт	1тт	0	1.		C		•		1
<sup>1</sup> H	чH	(:0111	nling	constants	tor	common	organic	compoi	inds
	<b>T T</b>	COup	Jung	combiantio	101	common	orguine	compou	AIIGO

Туре	J (Hz)	Туре	J (Hz)
>⊂ <sup>H</sup> <sub>H</sub>	12-15	H H 	2-9
$\begin{array}{c c} H & H \\ - C - (C)n - C - C \\ - C & - C \\ - C $	0	C <del>H3</del> CH2-x	6.5- 7.5
CH3 CH-X CH3	5.5- 7.0	H-C-C-H X Y	<ul> <li>aa 5-8</li> <li>ae 2-4</li> <li>ee 2-4</li> </ul>
C=C_H	0.5- 3	H C=C H	7-12
H_C=C_H	13-18	C=C_H	4-10
H_C=C_C-H	0.5- 2.5	HC=CC-H	0
C=C-C=C	9- 13	–C–C≡C−H H	2- 3
H H H	1- 3	C=C_H CO-H	2- 4
	<ul> <li>o 6- 9</li> <li>m 1- 3</li> <li>p 0- 1</li> </ul>	3 $2$ $1$	<ul> <li>1-2 1.6-2.0</li> <li>1-3 0.6-1.0</li> <li>1-4 1.3-1.8</li> <li>2-3 3.2-3.8</li> </ul>
$ \begin{array}{c} 3 \\ 4 \\ N \\ H \\ H \end{array} $	<ul> <li>1-2 2.0-2.6</li> <li>1-3 1.5-2.2</li> <li>1-4 1.8-2.3</li> <li>2-3 2.8-4.0</li> </ul>	$4 \sqrt{\frac{2}{1}}$	<ul> <li>1-2 4.6-5.8</li> <li>1-3 1.0-1.8</li> <li>1-4 2.1-3.3</li> <li>2-3 3.0-4.2</li> </ul>
4 2 5 N 1	<ul> <li>1-2 4.9-5.7</li> <li>1-3 1.6-2.6</li> <li>1-4 0.7-1.1</li> <li>1-5 0.2-0.5</li> <li>2-3 7.2-8.5</li> <li>2-4 1.4-1.9</li> </ul>	A H H H H b H C	a) 4.5 (gem) b) 6-10 (cis) c) 3-6 (trans)

## <sup>1</sup>H shifts

relativ to TMS	12	11	10	9	8	7	6	5	4	3	2	1	0	-1
H <sub>3</sub> C-Alkyl														
H <sub>3</sub> C-C-Hal														
H <sub>3</sub> C-C=C														
H <sub>3</sub> C-CC														
H <sub>3</sub> C-Aryl,-Heteroaryl														
H <sub>3</sub> C-CO														
H₃C-S-														
H <sub>3</sub> C-SO <sub>2</sub> -														
H₃C-N														
H <sub>3</sub> C-O-Alkyl														
H <sub>3</sub> C-O-Aryl, -O-CO-														
C-CH <sub>2</sub> -Alkyl														
Cyclopropane														
C-CH <sub>2</sub> -CO														
C-CH2-O-														
C-CH <sub>2</sub> -S														
C-CH <sub>2</sub> -NO <sub>2</sub>														
C-CH <sub>2</sub> -N														
C=C-CH <sub>2</sub> -C=C														
N-CH <sub>2</sub> -CO-														
-O-CH <sub>2</sub> -CO-														
-O-CH <sub>2</sub> -O-, -Aryl														

	12	11	10	9	8	7	6	5	4	3	2	1	0	-1
CH-Alkyl														
CH-Hal														
С-СН-О-														
C-CH-N														
CO-CH-C=C														
CH-Aryl,-NR-,-O-														
-CCH Alkine														
CH=C-														
Ar-H														
Alkyl-, Aryl-CHO														
Alkyl-OH														
Aryl-OH														
R-COOH														
Alkyl-SH														
Aryl-SH														
Alkyl-NH2, Alkyl2-NH														
Aryl-NH2, Aryl2-NH														
R-CO-NH-														
-CO-NH-CO														
	12	11	10	9	8	7	6	5	4	3	2	1	0	-1

## <sup>13</sup>C Chemical Shifts

relative to TMS	220	200	180	160	140	120	100	80	60	40	20	0	-20
H <sub>3</sub> C-C- primary													
H₃C-S-													
H₃C-N													
H <sub>3</sub> C-O-													
-H <sub>2</sub> C-C secondary													
Cyclopropanes													
-H <sub>2</sub> C-S-													
-H <sub>2</sub> C-N													
-H <sub>2</sub> C-O-													
-H <sub>2</sub> C-Hal								F	CI	Br	I		
>CH-C- tertiary													
>CH-S-													
>CH-N													
>CH-Hal							F	CI	Br	I			
C-C quarternary													
C-S-													
C-N													
C-O-													
C-Hal								CI	Br	I			

relative to TMS	220	200	180	160	140	120	100	80	60	40	20	0	-20
Alkines													
C=C=C Allenes													
C=C Alkenes													
Aromatic Compounds													
Heteroaromatic Compounds													
-S-CN Rhodanides													
-N=C=S Isothiocyanates													
-O-CN													
-N=C=O													
-CN													
-NC													
>C=N- Azomethines													
(-CO)2O Anhydrides													
-COOR													
-CONHR													
-(CO)2NR Imides													
-COOH													
-COCI													
-CHO													
>C=0													
relative to TMS	220	200	180	160	140	120	100	80	60	40	20	0	-20