Experiment 9: Proton Exchange of Pyruvic Acid *via* NMR

Procedure

CHE 347 TA: Alec Beaton

Introduction

In this experiment, we will use NMR spectroscopy to investigate the effect of H^+ concentration on the hydrolysis of pyruvic acid. We will use the linewidths of the proton resonances corresponding to pyruvic acid and to 2,2-dihydroxypropanoic acid to calculate the forward rate constant and the reverse rate constant, respectively. We will then combine this information to determine the overall rate constant for hydrolysis.

Objectives

- General introduction to NMR instrumentation

- General introduction to NMR data processing

- Use of NMR data to calculate kinetic information

Materials

- Pyruvic Acid
- D_2O
- HCl

Experiments

For these experiments, nine samples will be prepared of pyruvic acid in D_2O with varying amounts of H^+ concentration.

Sample No.	Vol. Pyruvic Acid (μL)	Vol. D2O (μL)	Vol. HCl (μL)
1	10	600	0
2	10	575	25
3	10	550	50
4	10	525	75
5	10	500	100
6	10	475	125
7	10	450	150
8	10	425	175
9	10	400	200

The TA has previously acquired ^{1}H NMR spectra on the 300 MHz which will be provided to you for these experiments.

During your assigned time slot, the TA will provide you with an introduction to NMR instrumentation, data acquisition, and processing, relevant to the experiment at hand.

References

Note: We do not follow the experiments verbatim in either of these references, but they provide good introductory information and background which will help you on the postlab. Both are available on blackboard.

(1) "NMR Study of a Reversible Hydrolysis Reaction"

(2) Socrates, G. Kinetic Study by NMR. *J. Chem. Educ.* **1967**, *44* (10), 575.

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Post-Lab

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Introductory Information:

1. What is NMR?
2. What are some uses and applications of NMR? Why is it important to study?
3. What is pyruvic acid? Where is it naturally found? Why is it important to study?
4. What is FWHM? How is it related to the values you will report?

Experimental Details:

1. Name the chemicals used in this experiment. **Calculate and provide the concentrations of HCl used in each solution.**
2. Briefly describe the process of conducting an NMR experiment (name the steps with brief description of each step, as discussed in lab)

Results:

1. Plot linewidth vs $[H^+]$ for the pyruvic acid proton resonance. Provide a linear fit.
2. Plot linewidth vs $[H^+]$ for the 2,2-dihydroxypropanoic acid proton resonance. Provide a linear fit.
3. Report results in a formatted table (**must include units**)
    - Forward rate constant (k_f)
    - Reverse rate constant (k_r)
    - Equilibrium constant (K_{eq})
    - Equilibrium constant (literature value: **0.70**)
    - Percent errors for equilibrium constant
4. Describe how you arrived at your values for k_r and k_f (i.e., show work including equations)
5. Describe how you arrived at your values for K_{eq} (i.e., show work including equations)
6. Include the NMR spectra for all 9 samples as an appendix to your submitted report

Discussion:

1. State/describe the expected trend in the NMR spectra as the concentration of HCl increases. To what extent do you observe this trend in the provided experimental NMR spectra (attached as an appendix)?

2. How does the experimental result for K_{eq} compare to the provided literature value? Which factors may have most contributed to any difference between the two?
3. Would you expect K_{eq} to change if the experiments were conducted on the 400 MHz NMR instead of the 300 MHz NMR? Why or why not?
4. Why was D_2O used instead of H_2O in these experiments?
5. Suggest possible improvements for repeating this lab in the future.

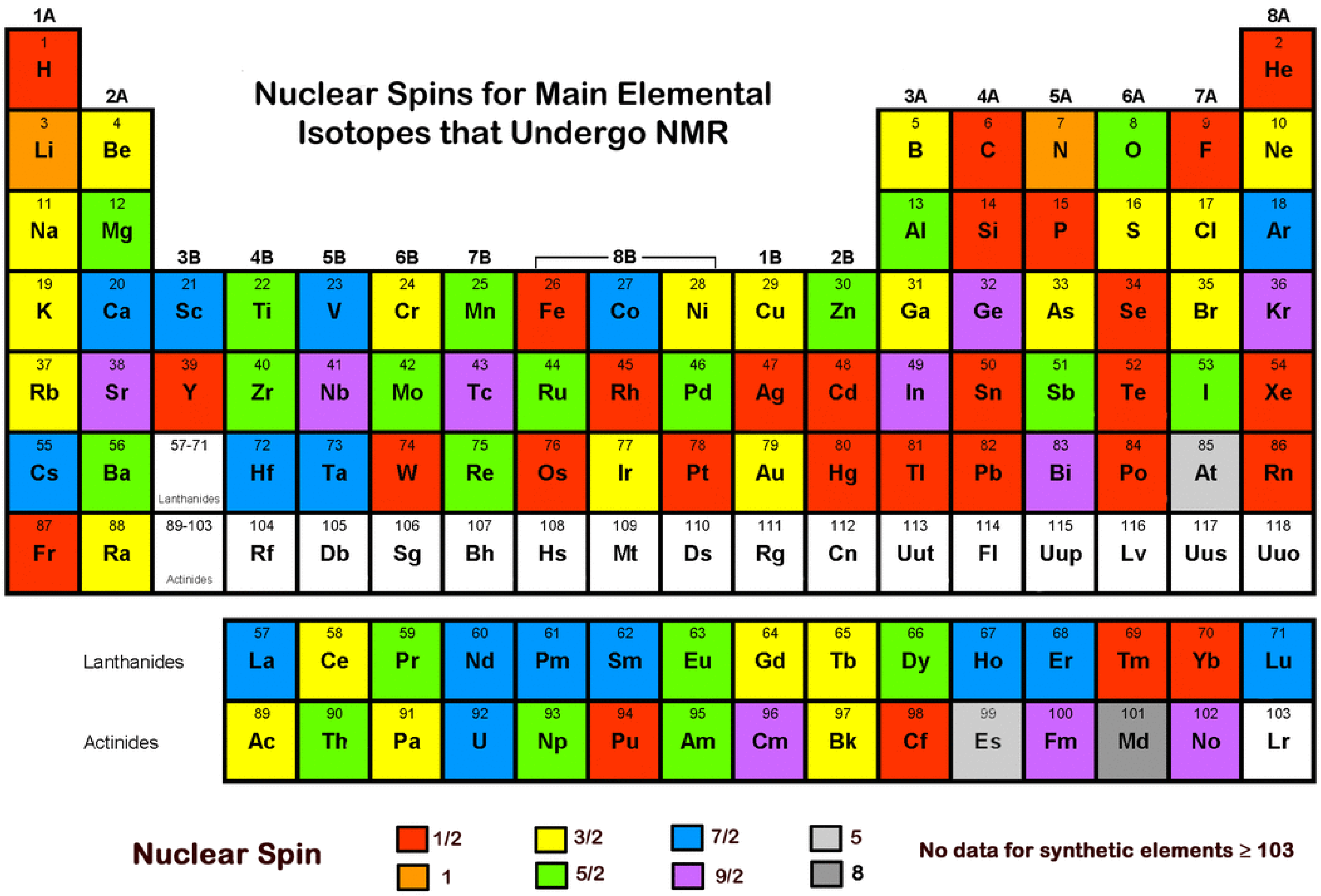
Experiment 9
(Companion Slides)

CHE 347

November 2021

Alec Beaton

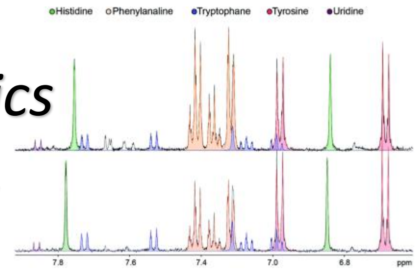
Periodic Table of NMR



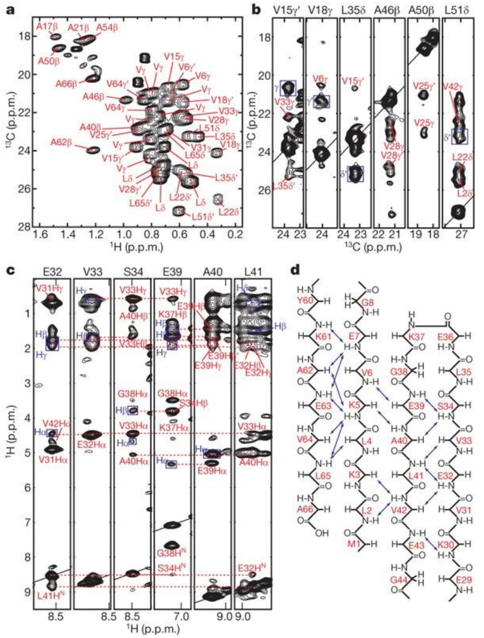
Modern NMR

metabolomics (forensics, medical)

https://doi.org/10.1039/C8AN01310A

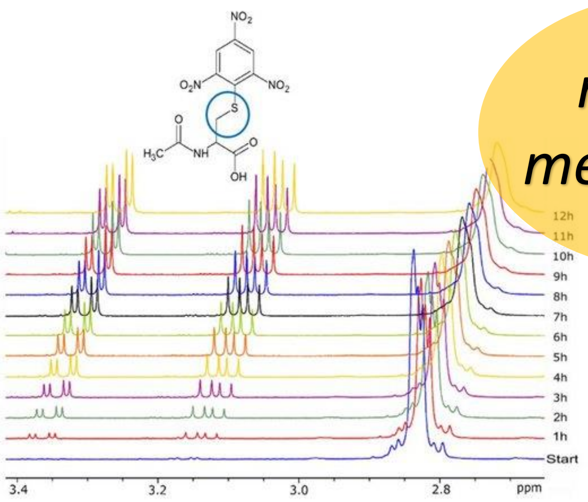


https://www.nature.com/articles/nature07814

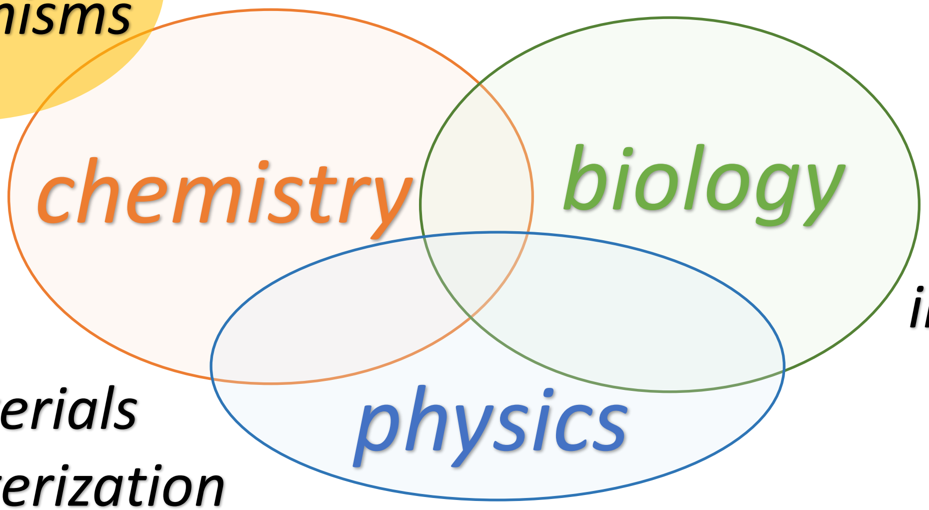


protein structures

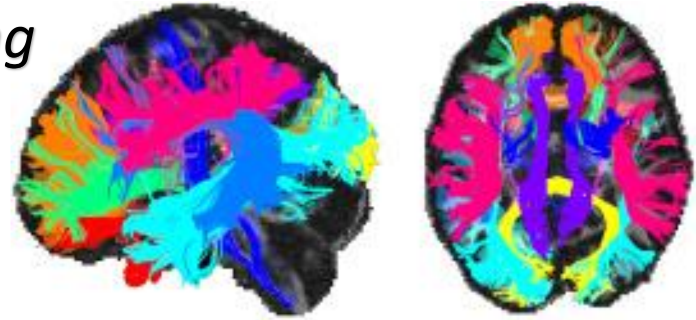
reaction mechanisms



https://tu-freiberg.de/en/

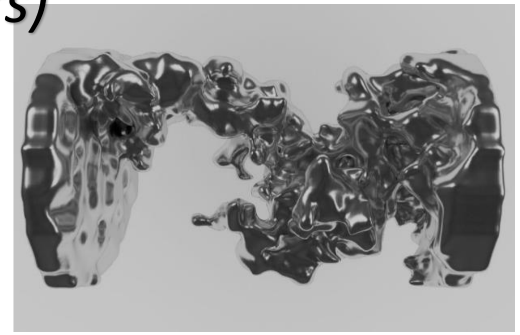


imaging

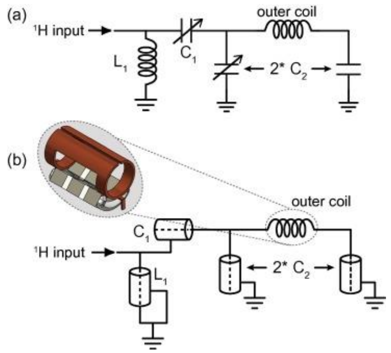


https://doi.org/10.1016/j.neuroimage.2017.10.058

materials characterization (batteries, polymers)



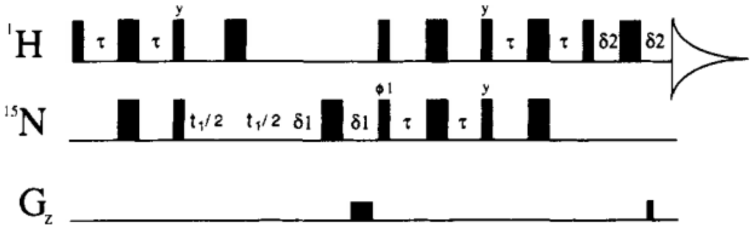
10.1073/pnas.1607903113



magnet/probe design

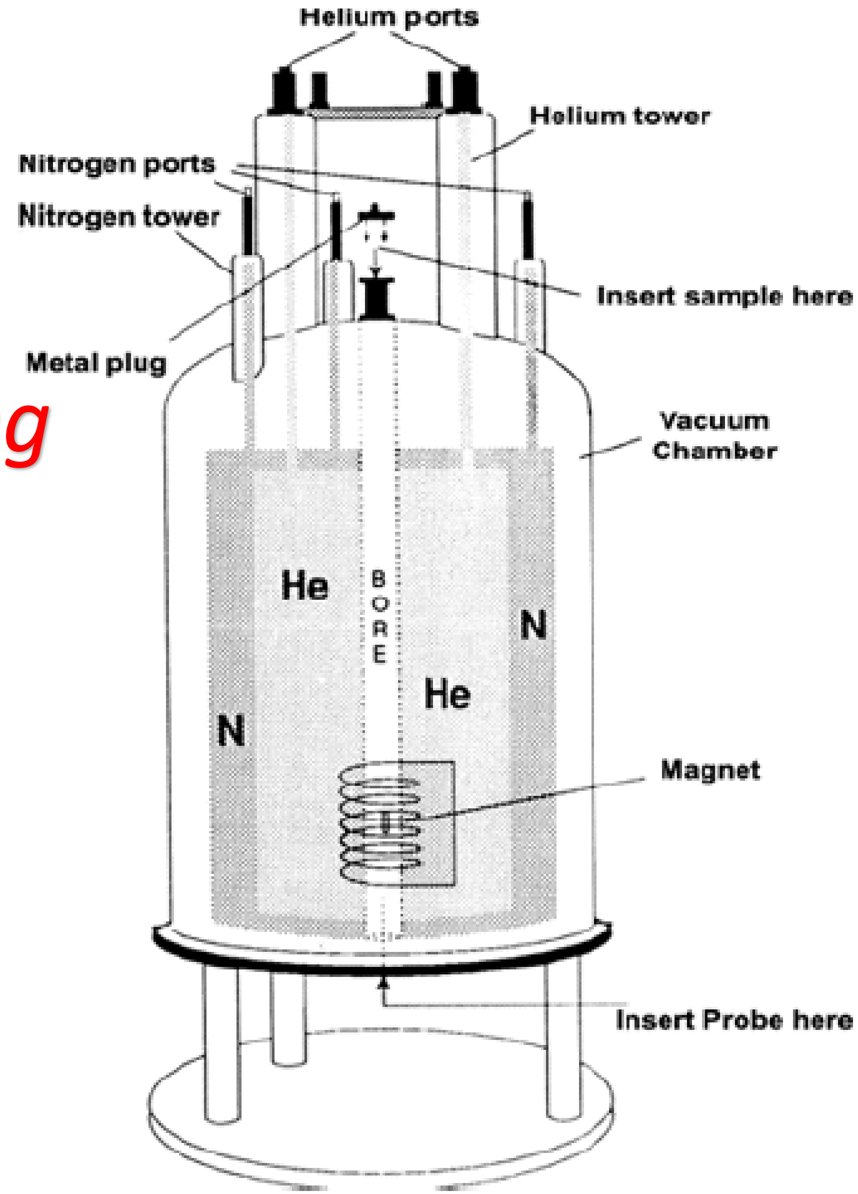
https://doi.org/10.1016/j.jmr.2017.10.002

theory



10.1021/ja00052a088

Super conducting magnets

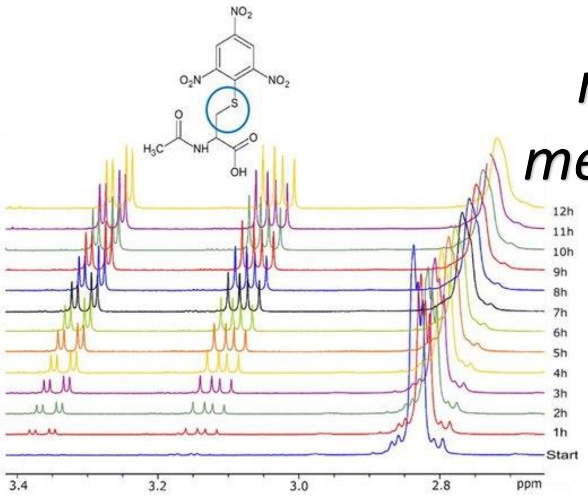


Electromagnet

Basic NMR Experiment

- Load sample
- Lock
- Shim
- Tune + Match
- Auto receiver gain
- Acquire

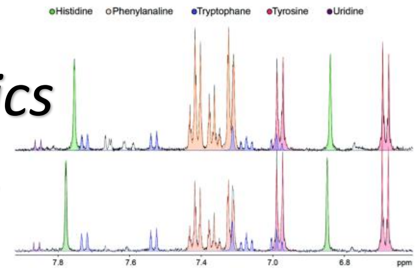
Modern NMR


https://tu-freiberg.de/en/

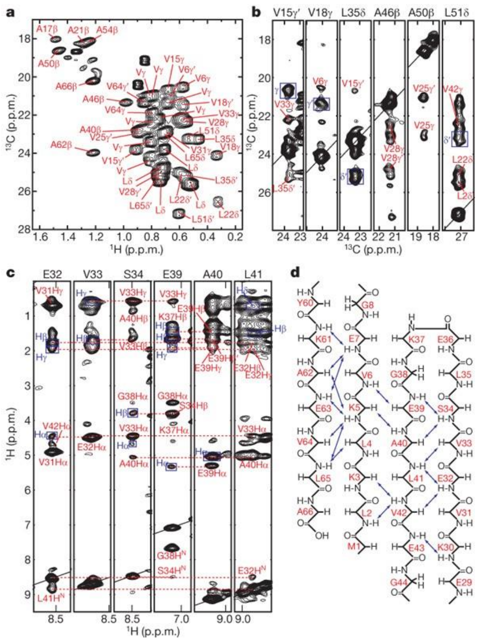
reaction mechanisms

https://doi.org/10.1039/C8AN01310A

metabolomics (forensics, medical)



https://www.nature.com/articles/nature07814



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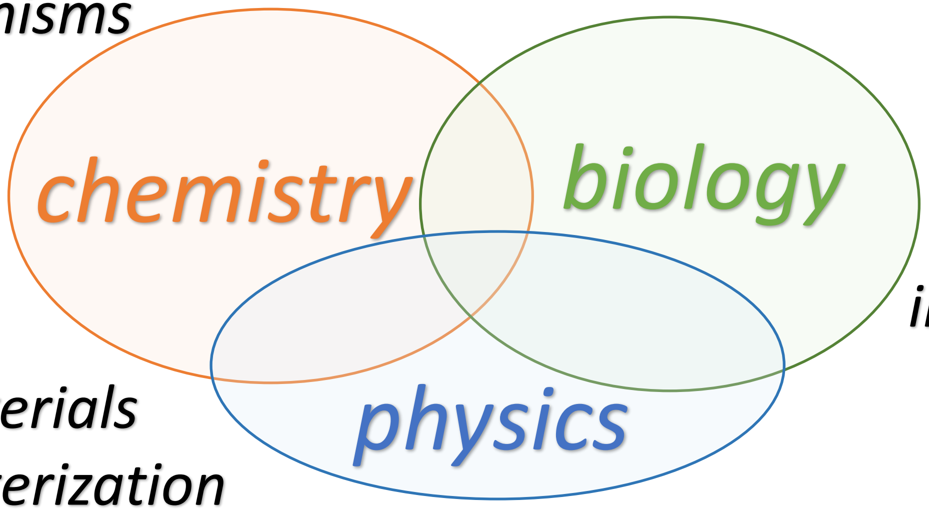
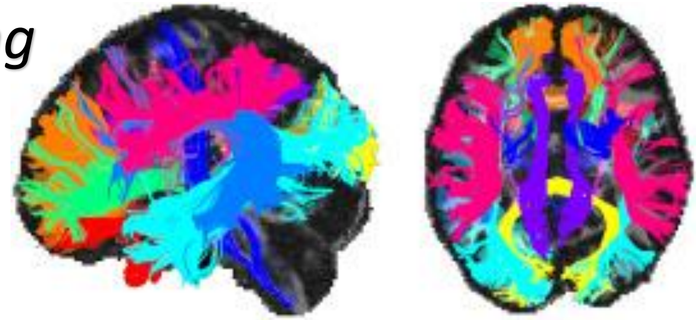


imaging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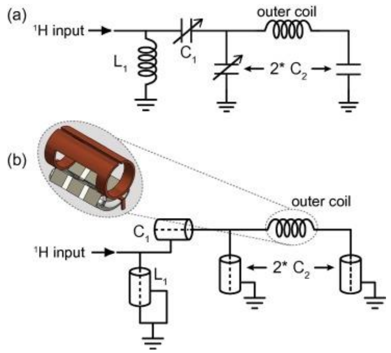
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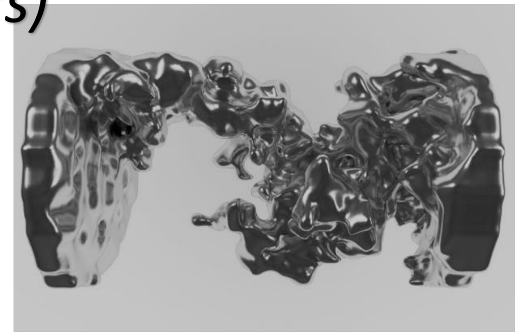
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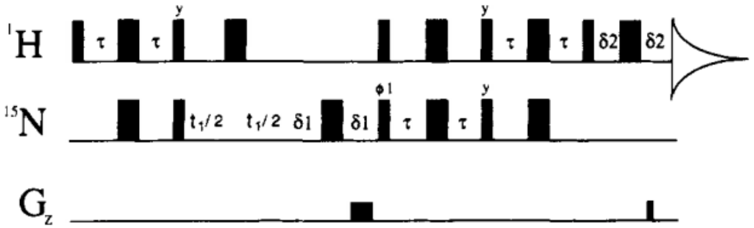
theory


10.1021/ja00052a088

Experiment 9: Proton Exchange of Pyruvic Acid *via* NMR – Rubric

Student:

Introductory Information (12 pts)

1. (/3 pts)
2. (/3 pts)
3. (/3 pts)
4. (/3 pts)

Total: (/ 12 pts)

Experimental Details (25 pts)

1. (/10 pts)
2. (/15 pts)

Total: (/ 25 pts)

Results (41 pts)

1. (/8 pts)
2. (/8 pts)
3. (/10 pts)
4. (/5 pts)
5. (/5 pts)
6. (/5 pts)

Total: (/ 41 pts)

Discussion (22 pts)

1. (/5 pts)
2. (/5 pts)
3. (/5 pts)
4. (/5 pts)
5. (/2 pts)

Total: (/ 22 pts)

Report Total: (/ 100 pts)

General Comments: