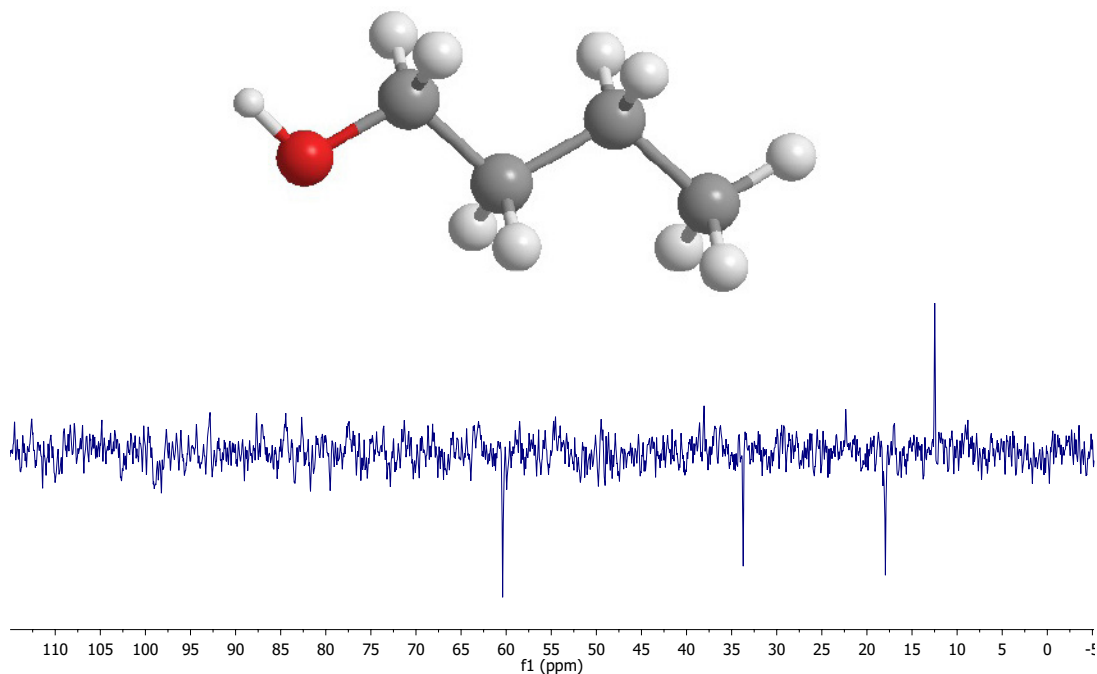


Introduction to ¹³C-NMR and DEPT – Identification of an Alcohol

DEPT 135



Contents

Objectives	1
Introduction	1
Experiment	2
Safety	2
Example Spectra	4
Propan-2-ol	6
Cyclohexanol	6
2-Methyl-2-propanol	7
Ethanol	7

Objectives

The identification of alcohols by NMR spectroscopy is aimed to introduce students to NMR spectroscopy early in their undergraduate career. The objectives of the experiment are for students to identify an alcohol using 1D ^{13}C -NMR and DEPT experiments and assign the peaks, reinforcing prior knowledge of electronegativity and naming organic compounds. This experiment allows students to acquire their own spectra in order to solve the structure of a relatively simple compound, with the opportunity to add in distillation to determine the boiling point of the unknown alcohol as an additional experimental technique.

Introduction

^1H -decoupled ^{13}C -NMR spectra are much simpler to interpret than ^1H -NMR spectra, and therefore is a good way to introduce students to NMR spectroscopy. There are three major concepts that students are introduced to early in their undergraduate studies that are required to interpret ^{13}C -NMR spectra: the number of distinct carbons in the structure, electronegativity and hybridisation. These concepts introduced in different areas of undergraduate chemistry can be combined to understand chemical shift and the number of resonances that appear in ^{13}C -NMR spectra.

This experiment utilises the identification of alcohols to introduce NMR spectroscopy. The use of alcohols allows students to correlate electronegativity with chemical shift and the peaks in the ^{13}C -NMR spectrum are well separated for straight forward interpretation. Alcohols are also a simple example for students to employ the nomenclature for naming organic compounds. There is also the option of introducing distillation into this laboratory as an experimental technique to purify and determine the boiling point of organic liquids. Because all of the alcohol samples are liquids, samples for NMR analysis can be easily prepared as students can acquire spectra of the neat liquids.

The Spinsolve Carbon system allows students to perform DEPT (**D**istortionless **E**nhancement by **P**olarisation **T**ransfer) experiments as well as traditional ^{13}C -NMR spectra. DEPT experiments distinguish carbon nuclei based on the number of protons attached to it. ^{13}C -NMR spectra show all carbons, DEPT-90 shows only CH's (3° carbons) and DEPT-135 shows protonated carbons, with CH and CH_3 's appearing positive and CH_2 's (2° carbons) appearing negative. Each student is able to identify their assigned alcohol from a class list based on the ^{13}C and DEPT spectra. If this experiment is a student's first exposure to NMR spectroscopy, the additional information of boiling point gives students confidence with their assignments.

Experiment

Students are provided with the class list, which contains the potential unknown alcohols. In the laboratory, students are assigned an unknown alcohol. The boiling point of this alcohol is determined by distillation, which also acts to purify the liquid (Figure 1). A 0.5 mL aliquot of the purified alcohol can be sampled directly into a 5 mm NMR tube. Students collect ^{13}C and DEPT data for their alcohol using the Spinsolve Carbon system and process the data to identify their unknown alcohol and assign the peaks in the spectrum.

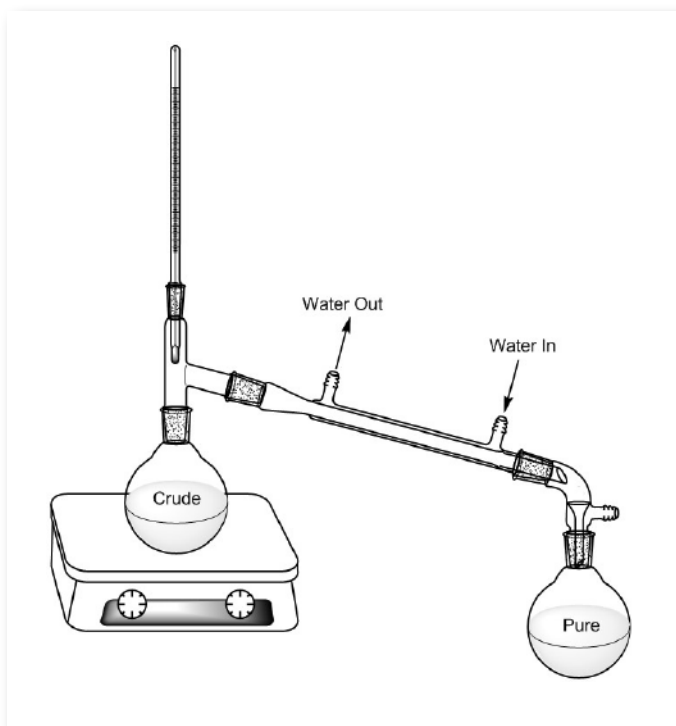


Figure 1: Distillation set-up.

Safety





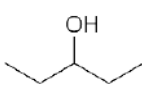
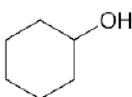

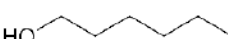
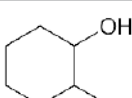
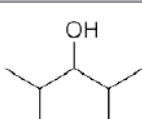
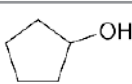
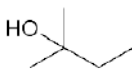
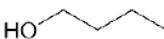
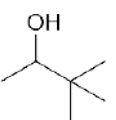
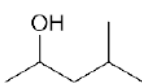
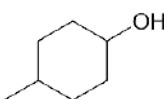
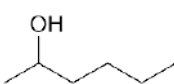
Some or all of the unknowns used in this experiment may be toxic and can be harmful if inhaled, comes into skin contact, or is ingested. Several of the alcohols are flammable, thus the unknowns should be kept away from flames and care must be taken when heating during distillation. With any unknown, all possible safety precautions should be taken.

Potential List of Unknowns

All of the alcohols in the list have a unique set of DEPT spectra, therefore there should be no ambiguity to the assignments. However, many of the compounds have the same number of resonances in the ^{13}C -NMR spectrum, which demonstrates how DEPT is a powerful tool in structural elucidation of compounds.

Tasks & Questions

1. Purify and determine the boiling point of the unknown alcohol using distillation.
2. Record the 1D ^{13}C -NMR, DEPT 135 and DEPT 90 spectra of your unknown alcohol.
3. Identify the unknown alcohol using the data collected and state your reasoning for the structure of your unknown.
4. Assign the peaks in the spectrum to carbon environments in the alcohol, explaining the chemical shifts of the carbon environments.

Compound	Structure	# Carbons	¹³ C	CH	CH ₂	CH ₃	Boiling Point °C
Ethanol		2	2	0	1	1	78
2-propanol		3	2	1	0	1	82
1-propanol		3	3	0	2	1	97
2-methyl-2-propanol		4	2	0	0	1	82
3-pentanol		5	3	1	1	1	115
cyclohexanol		6	4	1	3	0	160
1-pentanol		5	5	0	4	1	138
1-hexanol		6	6	0	5	1	157
2-methylcyclohexanol		7	7	2	4	1	165
2,4-dimethyl-3-pentanol		7	3	2	0	1	140
cyclopentanol		5	3	1	2	0	140
2-methyl-2-butanol		5	4	0	1	2	102
1-butanol		4	4	0	3	1	117
3,3-dimethyl-2-butanol		6	4	1	0	2	120
4-methyl-2-pentanol		6	5	2	1	2	132
4-methylcyclohexanol		7	5	2	2	1	170
2-hexanol		6	6	1	3	2	140

Example Spectra

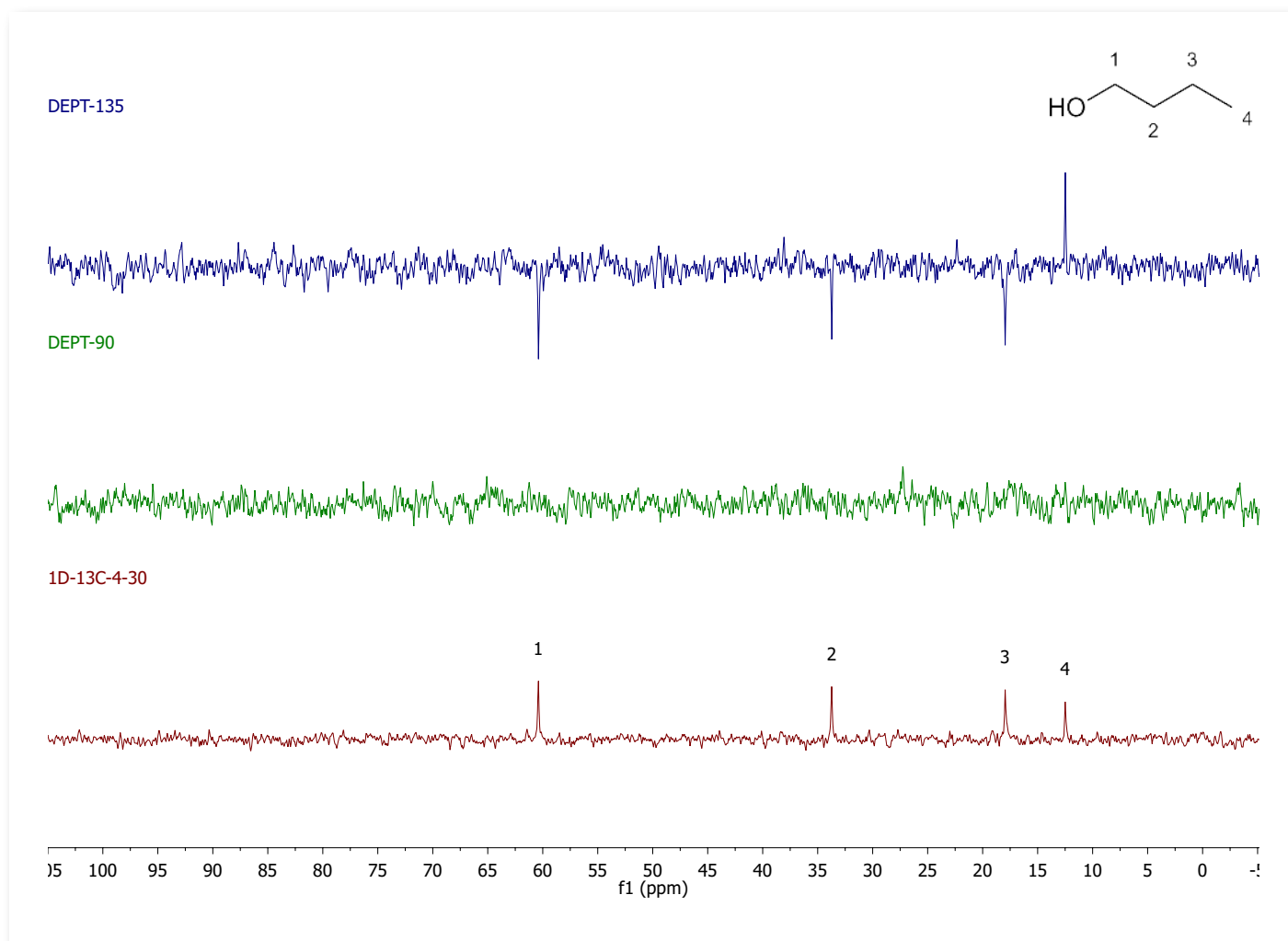
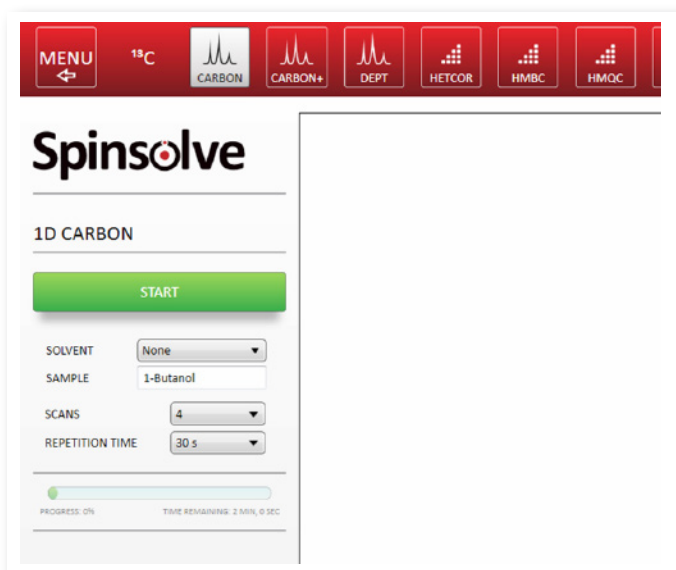


Figure 2: DEPT and 1D ^{13}C -NMR spectra of neat 1-butanol (4 scans).

The spectra obtained in Figure 2 for 1-butanol were carried out in two experiments and stacked during data processing. The 1D ^{13}C -NMR experiment was obtained using 4 scans with a repetition time of 30 seconds, therefore the spectrum was acquired in less than 2 minutes. Similarly, the DEPT experiment was obtained using 4 scans and a repetition time of 30 seconds. Because there are two spectra generated, the experiment took approximately 4 minutes to complete. Thus the total acquisition time for the spectra in Figure 2 was 6 minutes.

The Spinsolve software is quick and easy to

use, therefore there is very little additional time introduced by setting up the experiment. All that is required is that the experiment is selected using a series of buttons, the sample name is inputted and parameters are selected (Figure 3). Alternatively, the sequence of experiments may be automated using Scripts, so that students simply press 'Start'. The sample preparation is also very simple and quick, hence the total amount of time a student would be using the instrument should be around 10 minutes.



If a higher throughput is required, the 1D ^{13}C -NMR spectra can be obtained in 1 scan. This reduces the acquisition time to 30 seconds. Additionally, the repetition time may be reduced to 10 seconds for the DEPT experiments, reducing the total acquisition time to approximately 1.5 minutes (Figure 4). Note that a repetition time of 30 seconds is required for the 1D ^{13}C -NMR spectrum due to the long T_1 relaxation time of most carbon environments. The DEPT experiment relies on polarisation transfer from ^1H to ^{13}C . Therefore, its repetition time is governed by the much shorter T_1 of protons. If desired, the carbon T_1 can be reduced by adding a relaxation agent, which enables much faster repetition times.

Figure 3: Setting up a 1D ^{13}C -NMR spectrum in the Spinsolve software.

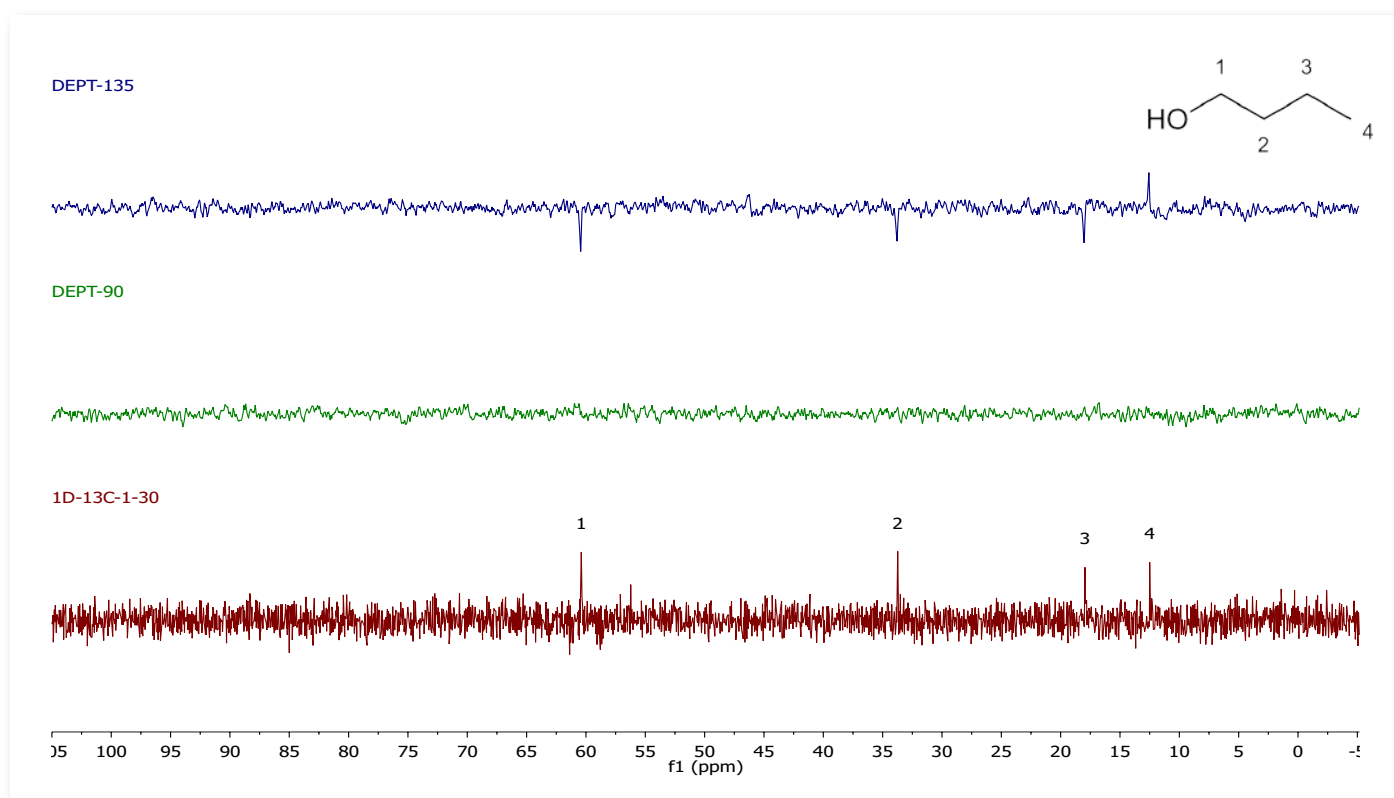


Figure 4: DEPT (4 scans, 10 s repetition time) and 1D ^{13}C -NMR (1 scan, 30 s repetition time) spectra of neat 1-butanol.

Whichever set of spectra is used, it can easily be seen that there are 4 carbon environments (1D- ^{13}C), there are no tertiary carbons (DEPT-90) and there are three CH_2 's and one CH_3

(DEPT-135). Students use this information combined with the principles of electronegativity to assign the chemical shifts in the molecule they have identified.

Propan-2-ol

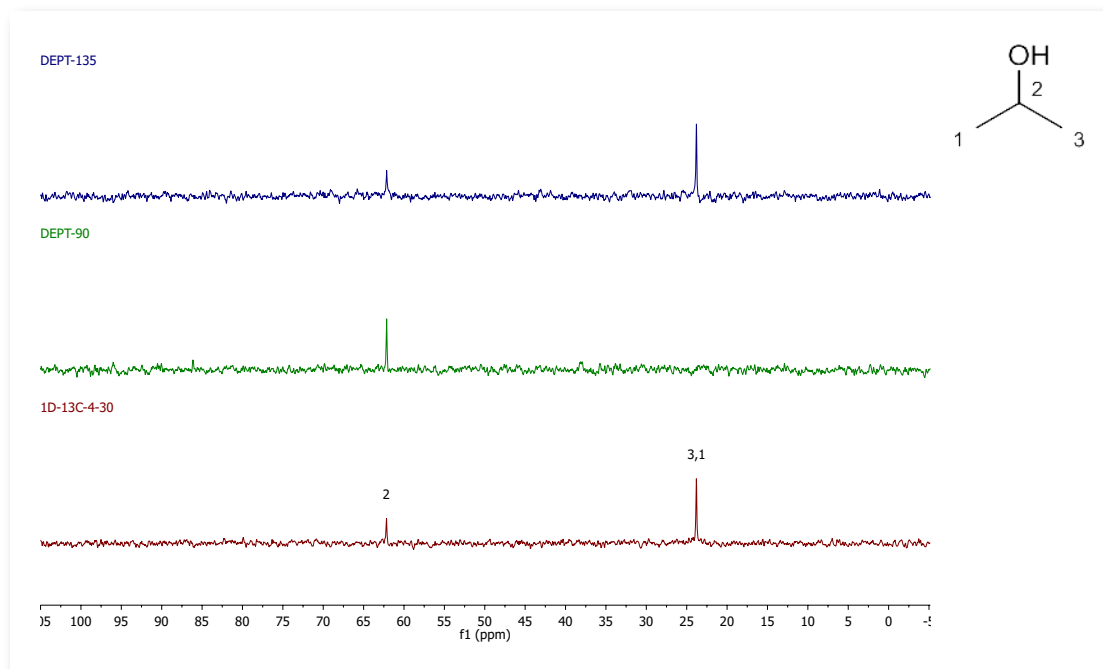


Figure 5: DEPT and 1D ^{13}C -NMR spectra of neat propan-2-ol (4 scans).

Cyclohexanol

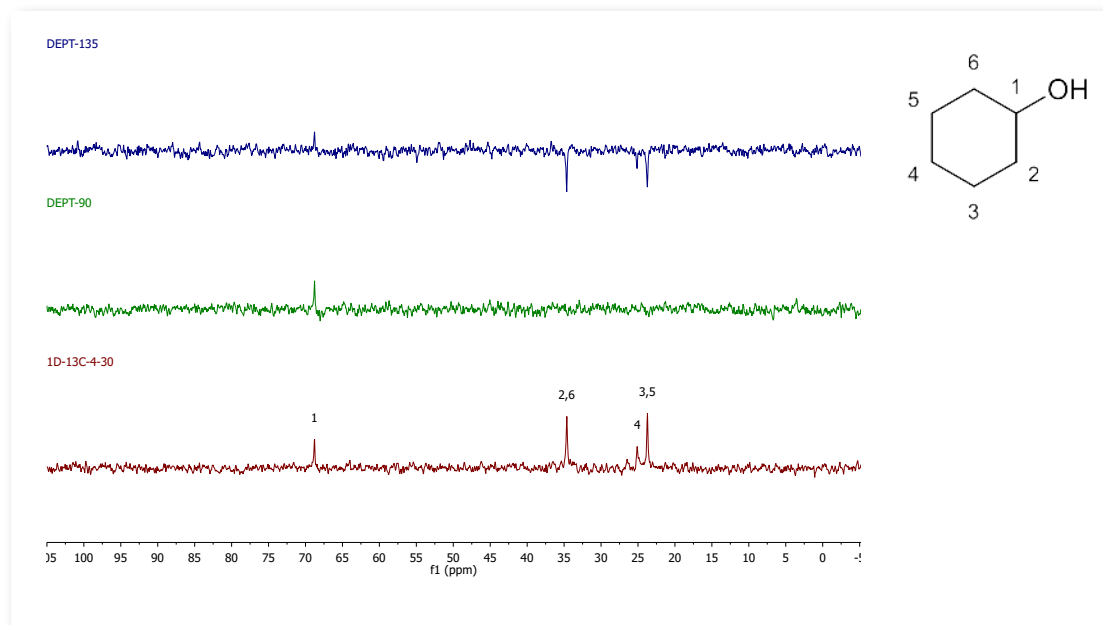


Figure 6: DEPT and 1D ^{13}C -NMR spectra of neat cyclohexanol (4 scans).

Propan-2-ol and cyclohexanol have an axis of symmetry about the hydroxyl group and therefore show fewer resonances in the ^{13}C -NMR spectrum than there are carbons in the molecule. This

encourages students to think about the concept of different chemical environments, recognising that symmetry causes multiple nuclei to have the same chemical shift.

2-Methyl-2-propanol

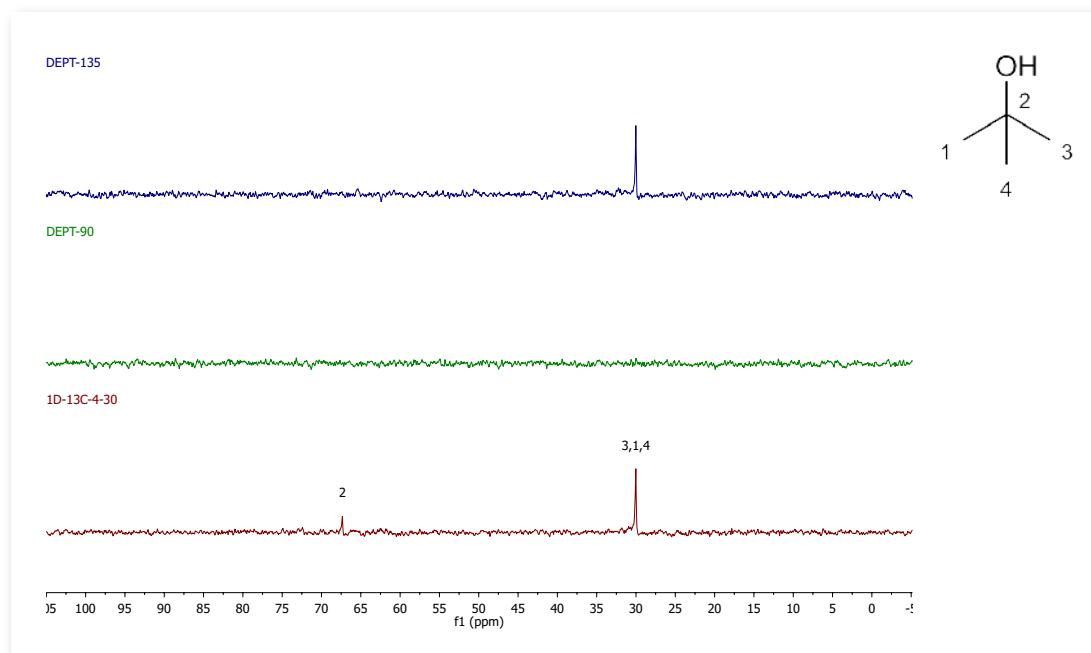


Figure 7: DEPT and 1D ^{13}C -NMR spectra of neat 2-methyl-2-propanol (4 scans).

2-Methyl-2-propanol is an example of a molecule with a quaternary carbon. This type of carbon appears in the ^{13}C -NMR spectrum, but since it is

not protonated does not appear in the DEPT spectra.

Ethanol

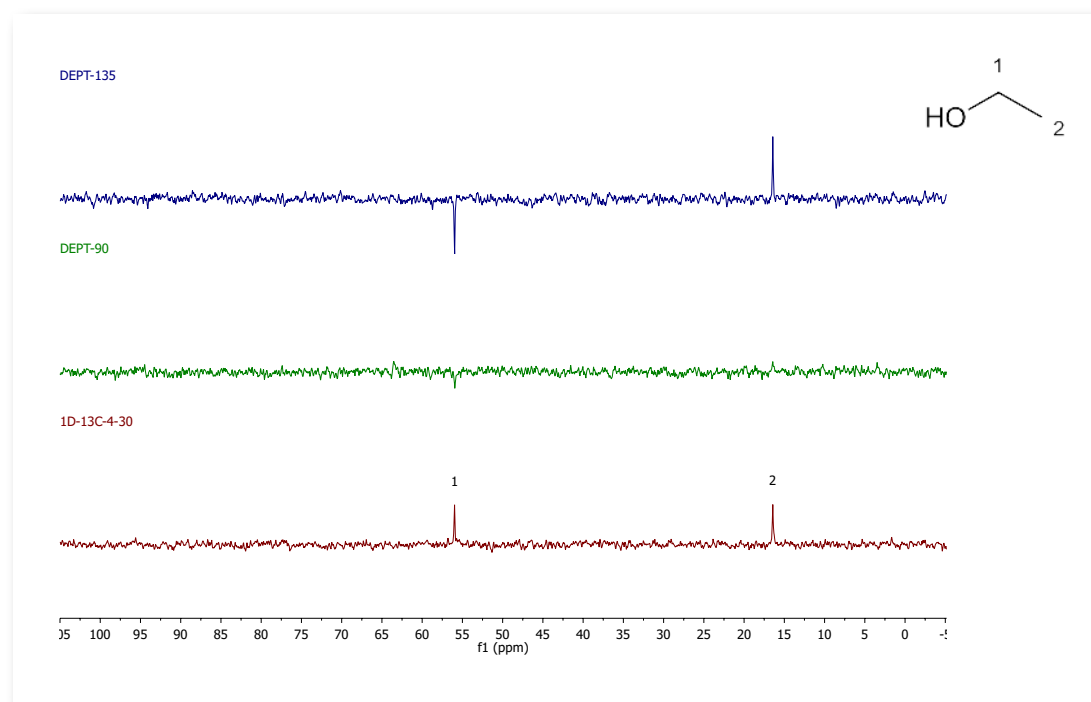


Figure 8: DEPT and 1D ^{13}C -NMR spectra of neat ethanol (4 scans).



Spinsolve[®]



References

- 1) P. H. Chamberlain, 'Identification of an Alcohol with ¹³C NMR Spectroscopy', *Journal of Chemical Education* **2013** 90 (10), 1365-1367.

CONTACT INFORMATION

For further information, please contact: sales@magritek.com

UNITED STATES

6440 Lusk Blvd (D108)
San Diego, CA 92121
Tel: (855) 667-6835
(855) NMR-MTEK

GERMANY

Pauwelsstr 19
52074 Aachen, Germany
Tel: +49 241 963 1420
Fax: +49 241 963 1429

NEW ZEALAND

32 Salamanca Road
Wellington 6012, NZ
Tel: +64 4 920 7671
Fax: +64 4 471 4665

Or visit our website www.magritek.com