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Resonance and its Applications

Conference Paper

Teaching Experiments Utilizing TeachSpin and 60 MHz Benchtop NMR Instruments

This paper explores three teaching experiments designed to illustrate key concepts in nuclear magnetic resonance (NMR) spectroscopy. Each experiment was designed with the intent to provide overlap between both chemistry's benchtop and physics' TeachSpin instrument. Unfortunately, due to the abrupt transition to online classes mid semester, each experiment will need to be tested, and most likely adequately refined, before they are able to be employed in the classroom.

Prior to experimentation, students should have a firm understanding of the physical and chemical theory behind nuclear magnetic resonance spectroscopy, inequivalent nuclei, shielding, chemical shifts and coupling constants. Students should also be comfortable using and analyzing data from the TeachSpin and benchtop NMR.

Experiment #1: Identifying Inequivalent Nuclei

The fluorinated samples provide a launching point for the identification of inequivalent nuclei using the TeachSpin NMR as flourine's magnetic moment is nearly identical to that of hydrogen. Subsequently, fluorine nuclei will produce clear and prominent signals that are easily identifiable within the spectra. Prior to implementing this experiment in the classroom, it would

be beneficial to obtain high resolution ^{19}F NMR spectra of each compound provided for accurate comparison[1]. Having the larger magnetic field strength data would not only be useful for comparison with the TeachSpin data but also clarify some discrepancies I found between the number of inequivalent nuclei identified by TeachSpin **[1]** (3) versus the number present in the molecular structure (5) of FC-70.

This could be attributed to a number of reasons. The fluorinated compounds provided with the instrument were difficult to find structural information for, as these complexes seemed to be used for industrial purposes rather than experimentation. Therefore, the molecular structures identified for these complexes could be incorrect. By obtaining high resolution spectral data for each complex, we will be able to more definitively elucidate chemical structure which allows students to more accurately interpret data from the physics instrument. Additionally, there are a number of nuclei which will report similar ppm (or MHz) values due to their local and chemical environments within the molecule. Because of the broad peaks put forth by the TeachSpin instrument, nuclei with similar values could be buried within one another, or the molecule could be rotating in such a way that we are receiving less signals than additionally anticipated.

These inconsistencies cannot fully be addressed until we have obtained the high resolution structural data and fully confirmed the chemical structure of each compound. In the table below, I have provided a chemical structure for each fluorinated compound, determined the number of inequivalent nuclei, and estimated approximate ppm values of each chemical shift for the structures given.

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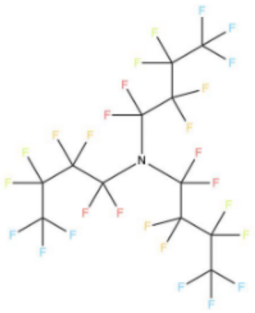
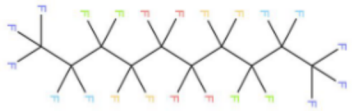
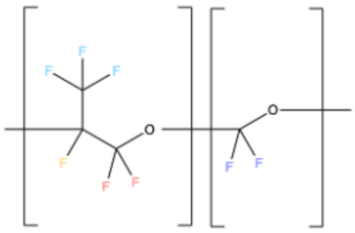
[1] If there is published data of these spectra, it was not easily found nor was it provided on the manufacturers (Sigma Aldrich, 3M, Look Chem, Galden) website

Compound Name	Chemical Structure	Anticipated ppm Values[2]
FC-43 Sigma-Aldrich		Fluorines closest to nitrogen: ~ -85 ppm C-F bonds:~ 81 - 82 ppm, F atoms closest to the nitrogen will be in the 82 ppm range (possibly slightly higher) while those further away will be closer to 81 ppm
FC-70 NIH Sigma-Aldrich		Fluorines closest to nitrogen: ~ -85 ppm C-F bonds: ~ 81 - 82 ppm, F atoms closest to the nitrogen will be in the 82 ppm range (possibly slightly higher) while those further away will be closer to 81 ppm
FC-770 Look Chem		All Fluorine atoms should be reported in the ~ 81 - 82 ppm range.
HT-110 Galden Information Sheet Look Chem		Fluorines bonded adjacent to oxygen: ~67 ppm All other Fluorine atoms: ~ 81 - 82 ppm

[2]The ppm values determined came from: F19 Shift Table

Objective: Students should be able to identify inequivalent nuclei and identify chemical shifts values from an obtained NMR spectrum.

Procedure:

1. Students will be given a fluorinated chemical sample and will obtain spectrum using the TeachSpin NMR

Example of FFT Spectra of FC-70 [1]

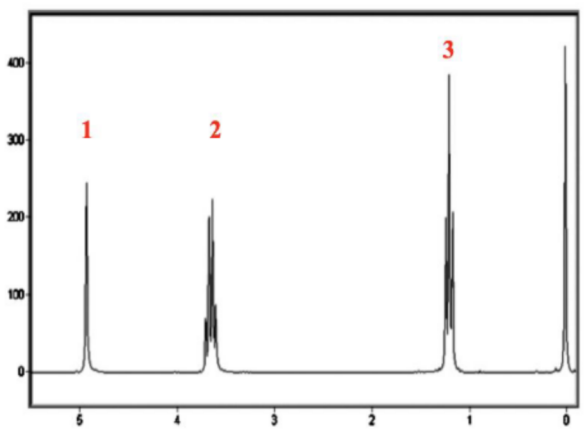
2. Students will then be asked to analyze the spectra and be asked to determine the number of inequivalent nuclei that is present within the molecule.
3. The resonance peaks of each will be calculated by the student and compared with values provided by the instructor (perhaps in both MHz and ppm for use later)
    - Ppm value can be calculated by $\delta = \frac{Instrument\ Frequency\ (Hz)}{Larmor\ Frequency\ of\ the\ nucleus}\ x\ 10^{6}$
4. Students will compare their results and determine any limitations / sources of error present within the experiment

Transition to Chemistry:

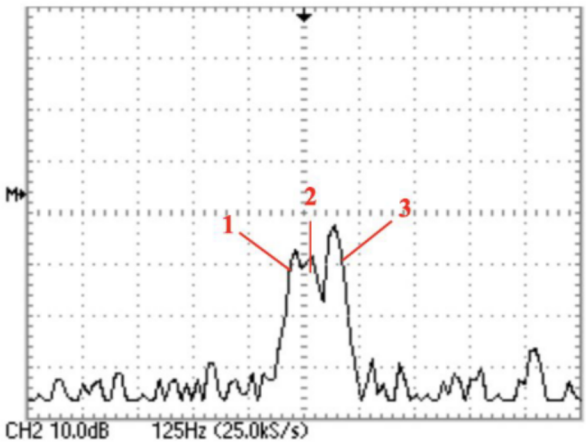
1. Students will be provided with the chemical structure of the compound previously analyzed and will be asked to determine the number of inequivalent nuclei within the molecule.
2. Given the calculated ppm values, students will be asked to determine which values are associated with which atoms
3. Students will then be given a copy of the high resolution NMR data of the same compound and be asked to compare that data with the teachspin data.
4. Students will then be asked to predict the ppm values of nuclei unobserved in the low-resolution spectra and provide an explanation on why they may not be present within the teachspin instrument.

Experiment #2 Chemical Shielding and Electronegativity

This second experiment has the propensity towards chemistry's benchtop NMR; however, it would be interesting to explore if the experiment could also be replicated on the TeachSpin instrument. The fast fourier transform (FFT) NMR data provided for an ethanol molecule in, *More Experiments with our New Pulsed NMR Spectrometer PS2-A* **[2]**, indicates that the TeachSpin instrument may not provide adequate clarity between peaks to determine chemical shielding. An ethanol molecule is relatively simple in structure, with only three inequivalent proton environments with adequate different chemical shifts to provide easily distinguishable peaks in the high resolution FFT NMR data. However, we can see in the TeachSpin data, there is significant overlap between all three peaks, and the protic hydrogen (1) and neighboring CH2 (2) signals are nearly indistinguishable. This is only amplified in the provided TeachSpin spectra of the much more complex molecule, toluene.



High Resolution NMR FFT Signal of Ethanol

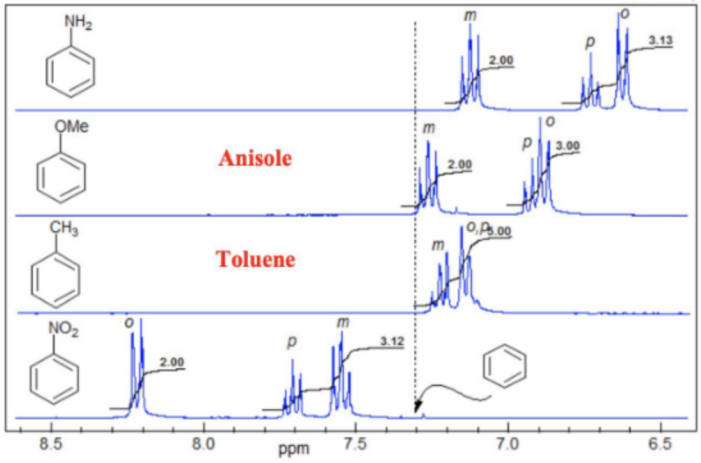


TeachSpin NMR FFT Signal of Ethanol

The premise of this experiment would be to take two molecules with similar chemical structures, but different heteroatoms, to demonstrate how electronegativity contributes to deshielding, which is illustrated in the overall NMR spectra of a molecule. By keeping the basic structural unit of the molecule the same, the number of peaks and the splitting will remain constant and students will only be observing the upfield and downfield shifts of the overall compound.

Aromatic compounds were chosen specifically for this experiment. Protons shift more downfield when an electronegative (EN) group is attached to the same or adjacent carbon. This is more easily seen in aromatic molecules as protons attached adjacent to the EN groups are pushed further upfield than in standard alkyl molecules. Thus, instead of seeing the difference in shifts around 0.05 ppm values, the difference in shifts will be much more apparent in the 0.5 ppm range. This difference *should* be recognized within chemistry's instrument and has the potential

to be within physics'[3]. For our experiment we will be using toluene and anisole, as these compounds are already in our chemical inventory.



^{1}H NMR spectra of several aromatic compounds [3]

Objective: Students will be able to determine how electronegativity relates to the shielding / deshielding of a molecule.

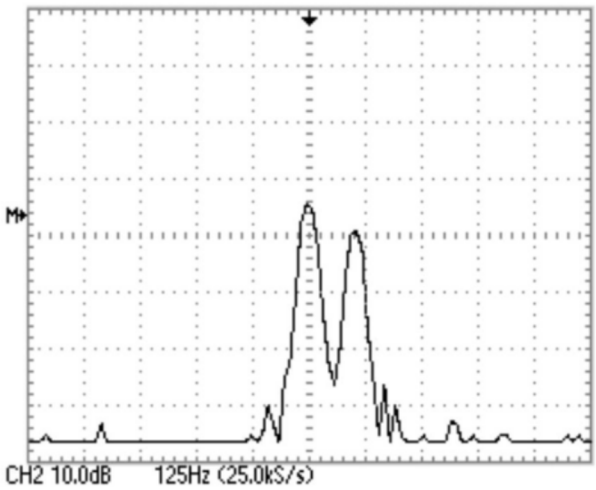
Procedure:

1. Students will be given the chemical structure of two compounds (toluene and anisole) and anticipate how the substituent will affect the chemical shifts of the adjacent hydrogen atoms (will they be pushed upstream or downstream) and predict their approximate ppm values
2. Students will then run a standard ^{1}H NMR spectra of each compound

[3] We have not tried to run simple aromatic molecules with our instrument, however, with more complex compounds we have run into some issues where we cannot distinguish between different proton environments situated around the aromatic molecule which we attribute as a drawback of our instruments magnetic field strength. Given these molecules are not very complex, hopefully we will not run into this issue.

3. Students will be asked to compare their predictions to the results provided by the instrument and then assign assign the appropriate protons to the peaks to the spectra in relation to how close they are located to the substituent

The TeachSpin NMR data has already been taken for toluene and shown promising results. Both the free induction decay (FID) and FFT spectra were taken and compared with the high resolution proton data from an instrument with an unspecified magnetic field strength **[2]**.



FFT of Toluene [2]

While the article specified the resolution is not as clear as one would use for chemical structure analysis, the splitting of the compound is observable, measurable and with agreement with the higher resolution data.

Experiment #3: Determining Coupling Constants

Another experiment that provides an interesting overlap between both instruments, and perhaps the limitations of magnet strength, would be the determination of coupling constants (J

values). It can be seen, in the spectra data referenced in the previous experiment, that the peak width of the TeachSpin instrument is so broad we cannot determine any structural information about the molecule besides a loose estimation of the number of inequivalent nuclei. We can further illustrate why this happens by taking the NMR data of the same compound with both instruments and determining the coupling constants provided by chemistry's benchtop instrument. We can then use these values to determine the coupling constants of the peaks within the TeachSpin instrument to provide an explanation for why splitting is not observed within the instrument.

Procedure:

1. A ^{1}H NMR of a simple molecule sample (TBD) will be taken with Chemistry's benchtop instrument.
2. The spectra can then be analyzed to determine J values by either using the data processing on the instrument or computer software such as TopSpin.
3. Students will then be asked to take the spectra of the same molecule using the TeachSpin instrument and correctly identify which peaks are equivalent between the two obtained spectra
4. Students will measure the peak width of the TeachSpin spectra at ½ height. If that value is equal to or less than the J value, splitting cannot be observed
    - J value can be determined by using J (Hz) = Pmm x instrument frequency
5. Students can then identify the splitting they are supposed to be observing as a specific fraction of the peak they are observing with the TeachSpin instrument.

References

[1] "More Experiments with Our New Pulsed NMR Spectrometer PS2-A." *News Letter of TeachSpin Inc.* , vol. 3, no. 3, Sept. 2008, https://drive.google.com/file/d/0B1nZP55TUGJMQmpLTl9SX0dVcHM/view.

[2] "Inequivalent Nuclei". *TeachSpin Inc.* https://www.teachspin.com/pulsed-nmr

[3] "5-HMR-2 Chemical Shift*". University of Wisconsin*, www.chem.wisc.edu/areas/reich/nmr/05-hmr-02-delta.htm