# 5.S: Summary

## Concepts & Vocabulary

### 5.1: Chapter Objectives and Preview of Nuclear Magnetic Resonance Spectroscopy

- Nuclear magnetic resonance spectroscopy is based on the function of nuclei as they interact with a magnetic field.

### 5.2 Theory of NMR

- Some types of atomic nuclei act as though they spin on their axis similar to the Earth.
- Atomic nuclei with even numbers of protons and neutrons have zero spin and all the other atoms with odd numbers have a non-zero spin.
- The magnetic moment of the nucleus acts as a tiny bar magnet.
- In the absence of an external magnetic field, each magnet is randomly oriented. However in the presence of an external magnetic field, the nuclear spins will either align with the magnetic field or oppose it.
- In order for the NMR experiment to work, a spin flip between the energy levels must occur.
- The local electronic environment surrounding the nucleus will slightly change the magnetic field experienced by the nucleus, which in turn will cause slight changes in the energy levels.
- Hydrogens attached to single or triple bonds are more shielded than alkenyl hydrogens due to position of induced magnetic fields of the electrons.
- Relaxation refers to the phenomenon of nuclei returning to their thermodynamically stable states after being excited to higher energy levels.

### 5.3 Instrumentation

- NMR spectroscopy works by varying the machine's emitted frequency over a small range while the sample is inside a constant magnetic field.
- The magnets used by NMR instruments are superconducting to create the magnetic field range from 6 to 24 T.
- A sample is inserted into the NMR probe, which sits in a uniform magnetic field, and is irradiated by radio wave frequency. A detector interprets the results.

### 5.4 Types of Protons

- There are homotopic, enantiotopic, and diastereotopic protons.
- Homotopic protons are identical protons and will be chemically equivalent. These will show up at the same location in NMR spectroscopy.
- Enantiotopic protons are chemically equivalent. These will show up at the same location in NMR spectroscopy.
- Diastereoptopic protons are different protons and will be chemically nonequivalent. These will show up at different locations in NMR spectroscopy.

### 5.5 Chemical Shift

- NMR spectra are displayed on a plot that shows the applied field strength increasing from left to right.
- The left side of the plot is low-field or downfield and the right side of the plot is high-field or upfield.
- The different local chemical environments surrounding any particular nuclei causes them to resonate at slightly different frequencies. This means that nuclei which have different chemical environments will show up in different regions of the NMR plot or spectrum.
- Chemical shift is dependent on the applied field of the spectrometer, so TMS is used as a standard in order to use the units parts per million (ppm). This allows scientists to talk about the same peak in the same units regardless of field strength.
- The main "things" that effect the shielding of a nucleus are electronegative of atoms, magnetic anisotropy of pi systems, and hydrogen bonding.
- Electron with-drawing groups can decrease the electron density at the nucleus, deshielding the nucleus, resulting in a larger chemical shift.
- The π electrons in a compound, when placed in a magnetic field, will move and generate their own magnetic field. The new magnetic field will have an effect on the shielding of atoms within the field.
- Protons that are involved in hydrogen bonding (*i.e.*-OH or -NH) are usually observed over a wide range of chemical shifts since hydrogen bonds are dynamic

## 5.6 Integration of Proton Spectra

- The area of a peak in a $^1H$ NMR is proportional to the number of hydrogens to which the peak corresponds.
- The integration curve appears as a series of steps with the height being proportional to the area of the corresponding absorption peak, and the number of protons responsible for the absorption.
- Integration can be used to determine the relative amounts of two or more compounds in a mixed sample.

## 5.7 Spin-Spin Splitting in Proton NMR spectra

- The split peaks (multiplets) arise because the magnetic field experienced by the protons of one group is influenced by the spin arrangements of the protons in an adjacent group.
- There is a recognizable pattern which is usually referred to as the n + 1 rule: if a set of hydrogens has n neighboring, non-equivalent hydrogens, it will be split into n + 1 subpeaks.
- Splitting occurs primarily between hydrogens that are separated by three bonds.
- The spin-spin coupling effect is quantified by the coupling constant, $J$. The coupling constant is simply the difference, expressed in Hz (not ppm), between two adjacent sub-peaks in a split signal.

## 5.8 More Complex Spin-Spin Splitting Patterns

- When a proton is coupled to two different neighboring proton sets with identical or very close coupling constants, the splitting pattern that emerges often appears to follow the simple `n + 1 rule` of non-complex splitting.
- If the set of protons is coupled to two or more sets of nonequivalent neighbors, the result is complex coupling.
- Complex coupling occurs when the coupling constants are different from each other on the neighboring protons.
- The stronger our magnet is, the more resolution we get in our spectrum. This means a clearer picture to gather more information.

## 5.9 Uses of $^1H$ NMR Spectroscopy

- Nuclear magnetic resonance imaging (MRI) is an important medical diagnostic tool developed from NMR spectroscopy.
- Scientists use NMR spectroscopy to determine the structure of a molecule.

## Skills to Master

- Skill 5.1 Distinguish between different types of protons in a molecule.
- Skill 5.2 Estimate the chemical shift of protons.
- Skill 5.3 Know which protons will be more downfield.
- Skill 5.4 Determine the ratio of different types of protons present in an organic compound.
- Skill 5.5 Provide a splitting diagram for a proton.
- Skill 5.6 Predict splitting patterns using a splitting diagram or the n + 1 rule.
- Skill 5.7 Interpret complex splitting in a spectrum.
- Skill 5.8 Solve unknown structure determination problems with $^1H$ NMR spectroscopy.

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