

13.S: STRUCTURE DETERMINATION - NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (SUMMARY)

CONCEPTS & VOCABULARY

13.1 Nuclear Magnetic Resonance Spectroscopy

- An applied magnetic field orients nuclei from random to aligned with or against the field. The nuclei absorb EM radiation of a frequency with energy that matches this energy gap.

13.2 The Nature of NMR Absorptions

- Nuclei in an applied field can align with the magnetic field (+1/2) or against the magnetic field (-1/2). The difference in the energy of these two states is the resonant frequency of that atom.
- To allow comparison between NMR spectra from instruments of differing field strength, the x-axis is reported as chemical shift, rather than frequency.
- **Chemical shift** is defined as the frequency of absorbance (in Hz) divided by the resonant frequency of the instrument (in MHz), thus the units are PPM (parts per million).
- Tetramethylsilane is used as a standard reference with its **chemical shift** set to 0 PPM (since these protons are highly shielded).
- Higher **chemical shifts** are called downfield, while lower shifts are called upfield.
- Nearby electrons shield the nuclei from the induced magnetic field, thus reducing their chemical shift. Atoms of higher electronegativity pull some of this electron density away from the nuclei causing increased **chemical shift**. This is called **deshielding**.

13.3 The Chemical Shift

- Pi electrons in a compound generate their own magnetic field that influences shielding of nearby atoms. This is most clearly exemplified by benzene protons that are highly deshielded (chemical shifts of 6.5-8 PPM).
- Protons that are involved in hydrogen bonding have variable chemical shifts and often do not absorb at one specific frequency, leading to broader peaks.

13.4 Chemical Shifts in ^1H NMR Spectroscopy

- Chemical shifts of protons are shifted upfield (higher ppm) by electronegative groups attached to the same carbon (and to a lesser effect when attached to nearby carbons).
- Aromatic protons appear between 6.5 and 8 ppm.
- Chemical shifts of O-H and N-H bonds vary with temperature and concentration.

13.5 Integration of ^1H NMR Absorptions - Proton Counting

- The area under a ^1H NMR signal is proportional to the number of hydrogens that caused the signal.

13.6 Spin-Spin Splitting in ^1H NMR Spectra

- ^1H signals are split into multiple peaks by neighboring H atoms whose spins can add to or subtract from the magnetic field.
- Spin-spin coupling yields $n+1$ peaks where n is the number of neighboring protons.
- Multiplets formed from spin-spin splitting follow specific symmetry based on the number of neighboring protons.
- The distance between peaks in a signal are called coupling constants.

13.7 ^1H NMR Spectroscopy and Proton Equivalence

- Equivalent protons (protons in identical electrical environments) only give 1 signal.
- To determine the number of ^1H NMR signals expected, symmetry of a molecule needs to be examined to find equivalent protons.
- Protons with different stereochemistry are not equivalent.
- Protons on chiral molecules that are diastereotopic (would create a diastereomer if replaced) are not equivalent.

13.8 More Complex Spin-Spin Splitting Patterns

- ^1H NMR signals can overlap making interpretation more difficult.
- Signals can distort where the peaks are not completely symmetrical in shape.
- When neighboring protons are nonequivalent, the coupling constant can be different leading to complex sets of peaks.
- Some complex multiplets can be identified such as a doublet of doublets, but others cannot and are referred to as multiplets.

13.9 Uses of ^1H NMR Spectroscopy

- ^1H NMR can help identify components of a mixture or determine which product was formed in a reaction.

13.10 ^{13}C NMR Spectroscopy - Signal Averaging and FT-NMR

- NMR signals for ^{13}C NMR are much weaker than for ^1H , requiring higher sample concentration and averaging of many scans (hundreds or even thousands).
- **Signal averaging** increases signal-to-noise ratio when running multiple scans in NMR.
- **Fourier Transform** NMR allows the entire spectrum to be acquired at once, rather than one frequency at a time.

13.11 Characteristics of ^{13}C NMR Spectroscopy

- Chemical shifts for ^{13}C NMR are spread over a wider range of frequencies (0-200 ppm).
- Carbons with sp^2 hybridization are shifted far downfield
- Since it is exceptionally rare to have two ^{13}C atoms adjacent to one another, there is no spin-spin coupling in ^{13}C NMR.
- Coupling constants between carbons and hydrogens are large and make interpretation of ^{13}C NMR spectra difficult, so most spectra are run using broadband decoupling. This leads to all signals in ^{13}C NMR appearing as singlets.

13.12 DEPT ^{13}C NMR Spectroscopy

- ^{13}C NMR DEPT experiments are used to identify the number of attached hydrogens each carbon has.

13.13 Uses of ^{13}C NMR Spectroscopy

SKILLS TO MASTER

- Skill 13.1 Interpretation of ^1H NMR Spectra.
- Skill 13.2 Interpretation of ^{13}C NMR Spectra.

MEMORIZATION TASKS (MT)

MT 13.1 Memorize chemical shifts patterns in ^1H NMR.

MT 13.2 Memorize spin-spin splitting patterns

MT 13.3 Memorize chemical shift patterns in ^{13}C NMR.

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