

NMR Spectroscopy I

Reading: Wade chapter 13, sections 13-1- 13-7

Study Problems: 13-35, 13-47

Key Concepts and Skills:

- Given a structure, determine which protons are equivalent and which are non-equivalent, predict the number of signals and their approximate chemical shift
- Given the chemical shifts of absorptions, suggest likely types of protons.
- Use integral traces to determine the relative numbers of different types of protons.

Lecture Topics:

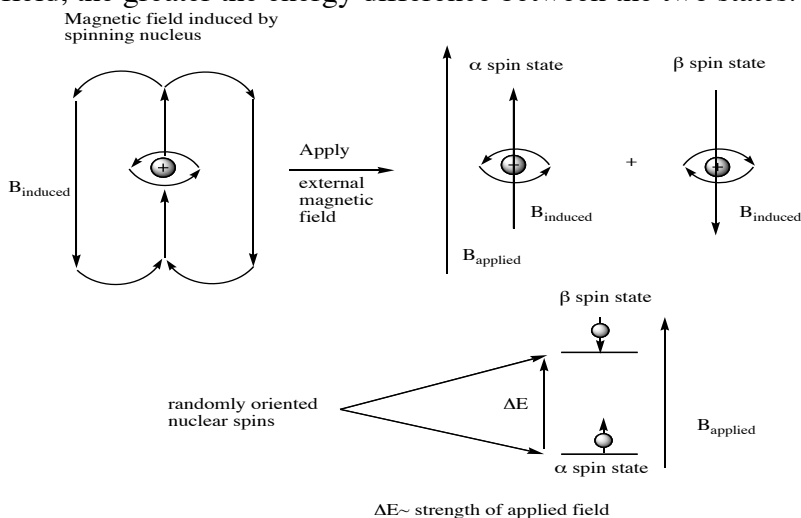
I. Theory of NMR

Nuclear Magnetic Resonance Spectroscopy (NMR) is a form of spectroscopy that measures the absorption of radio-frequency energy by nuclei in a magnetic field. It is the single most useful technique for the detailed structural analysis of organic molecules.

Background

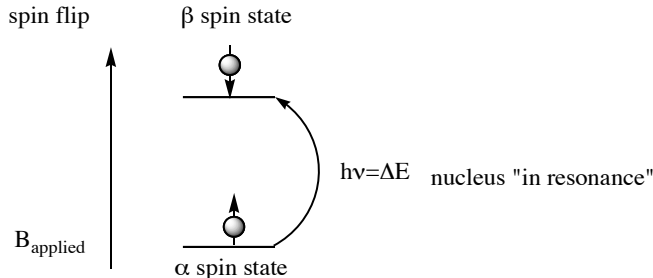
A nucleus with an odd atomic number or an odd mass number has a nuclear spin that can be observed by NMR spectrometers.

The proton (^1H) has a such a spin, and it can be viewed as a rotating sphere of positive charge \rightarrow generates a magnetic field. When an external magnetic field is applied, the nuclear spin can align itself in two ways: with its induced magnetic field aligned in the direction of the applied magnetic field (lower energy, call the α -spin state) or with its induced magnetic field aligned in the opposite direction of the applied magnetic field (a higher energy state referred to as the β -spin state). The difference in energy (ΔE) between the α and β spin states depends on the strength of the applied magnetic field; the stronger the magnetic field, the greater the energy difference between the two states.



Thus, $\Delta E \sim B_{\text{applied}}$. The absorption of a photon of correct energy, $h\nu$, causes the proton to spin-flip from the lower energy α -spin state to the higher energy β -spin state. At this

point, the nucleus is said to be “in resonance” and its absorption of energy is detected by the NMR spectrometer.



Proton resonance occurs in the radiofrequency range. Note that this frequency corresponds to the strength of the applied magnetic field, and is specific to a given nucleus. The gyromagnetic ratio γ is a constant that depends on the magnetic moment of the nucleus under study (note the ^{13}C has a γ value 1/4 that of the proton).

$$\Delta E = h\nu = (\gamma h/2\pi) B_{\text{applied}}$$

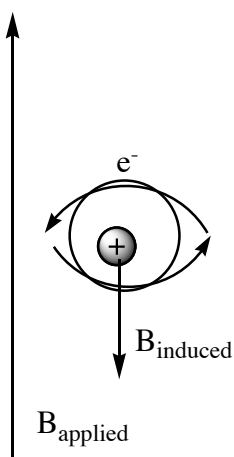
$$\nu = (\gamma / 2\pi) B_{\text{applied}}$$

NMR spectrometers typically operate at radiofrequencies of 200MHz, 400MHz, 500MHz, and 600MHz. **Remember, the stronger the field, the greater the value of ΔE and the higher the radiofrequency required to bring protons into resonance.**

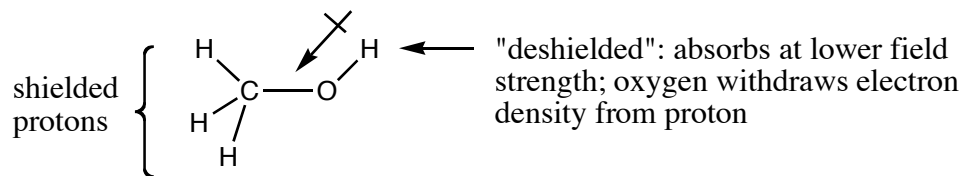
II. Magnetic shielding

Nuclei are surrounded by electrons that circulate and generate a small induced magnetic field that opposes the externally applied field. Thus, the net magnetic field at the nucleus is weaker than the applied field, and the nucleus is “shielded”. As a result, the applied field must be increased for resonance to occur at a given radiofrequency. Thus,

$$B_{\text{effective}} = B_{\text{external}} - B_{\text{shielding}}$$



Protons in different chemical environments are shielded by different amounts. For example in methanol, there are two types of protons: the hydrogen attached to O, and the hydrogens attached to C. Because oxygen is an electronegative element, it withdraws electron-density from the hydrogen atom to which it is directly attached, therefore the hydroxyl proton is “deshielded” and comes to resonance at a lower field strength than the protons which are attached to carbon. The protons attached to carbon are said to be “shielded”.



In an NMR spectrum, we can tell:

1. the number of different absorptions, which implies how many different types of protons are present in a given molecule
2. the amount of shielding often implies the electronic structure of the molecule close to each type of proton
3. the intensity of a signal (area of the peak) implies how many of each type of proton are present
4. The splitting of the signals gives information about the number and orientation of other nearby protons.

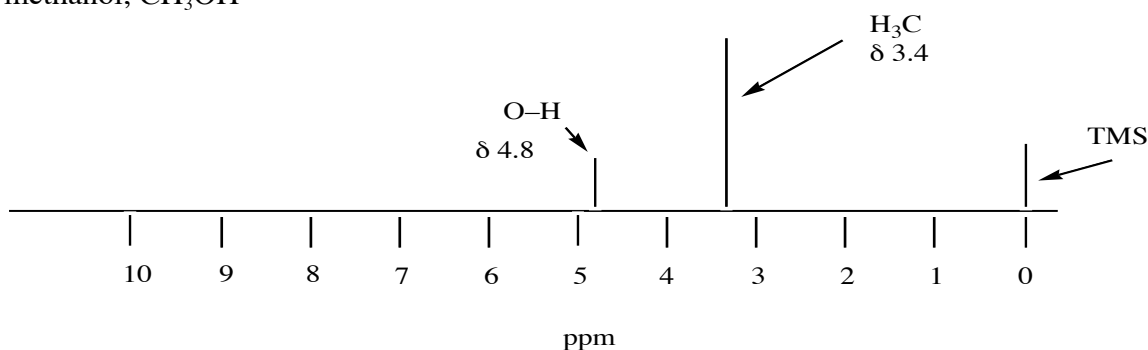
Note: an NMR spectrometer must be equipped to vary the field strength to bring protons with different amounts of shielding into resonance at a given radiofrequency.

III. Chemical Shift

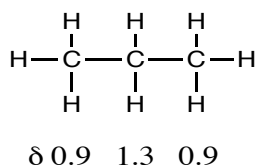
The variation in the positions of NMR absorptions, arising from electronic shielding and deshielding, and called chemical shifts. Chemical shift is defined as the difference (in parts per million, ppm) between the resonance frequency of the proton being observed and that of tetramethylsilane TMS. The hydrogens in tetramethylsilane are well shielded and electron rich, leading to a particularly high-field absorption defined as 0 ppm. Most NMR absorptions are downfield (absorbing at lower field) of TMS. The ppm value is a unitless fraction of the total applied field:

Chemical shift (ppm) = shift downfield from TMS (Hz) / total spectrometer frequency (MHz)

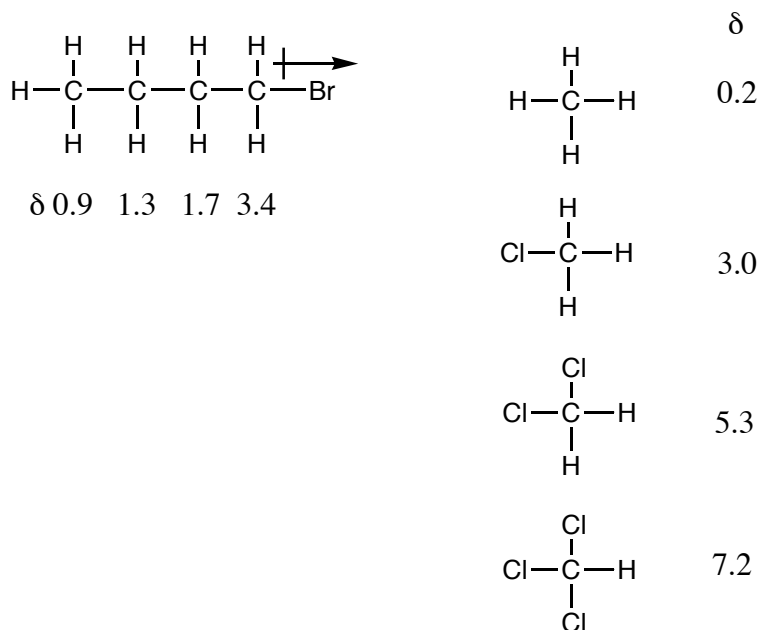
As a result, the chemical shift of a given proton is the same regardless of the operating field and frequency of the spectrometer. Let's take a look at the NMR spectrum of methanol, CH₃OH



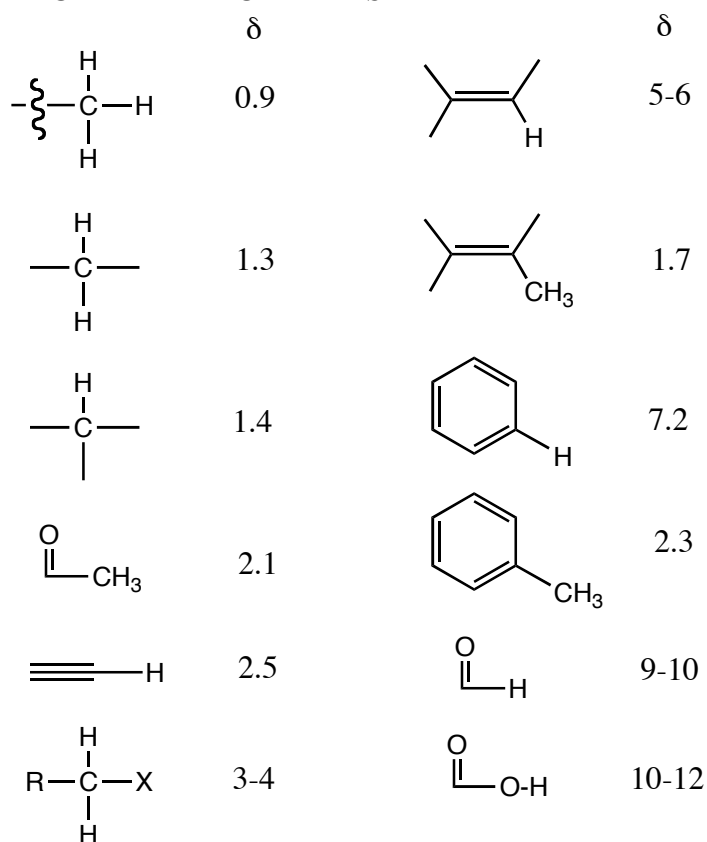
Both OH and CH₃ show deshielding effects of oxygen. Compare the ppm values listed above with those for a typical alkane:



Note that the chemical shift of the protons depends on the electronegativity of the attached substituent. The effect of electron-withdrawing substituents decreases with increasing distance. An additive effect of halides on chemical shifts is observed:



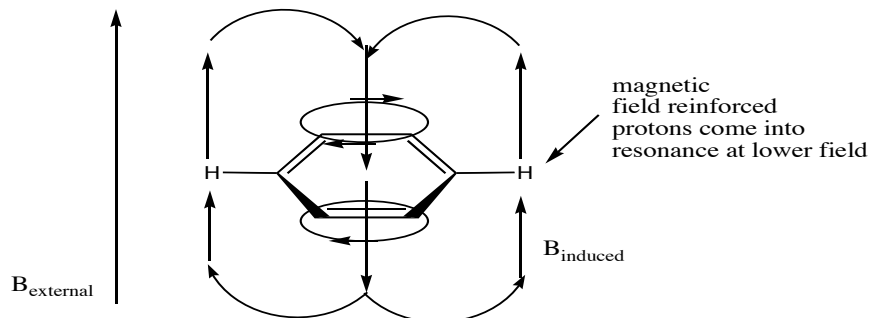
Following are Some Characteristic Chemical Shifts:



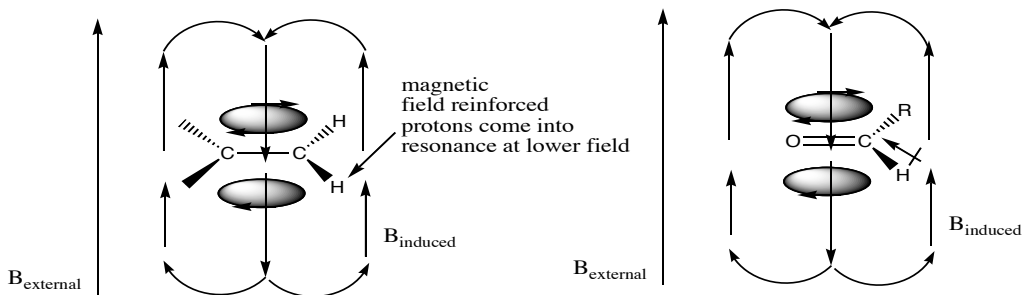
IV. Explanation of some important chemical shifts

Vinyl and aromatic protons

Large deshielding effects are observed for vinyl and aromatic protons. In aromatic rings, a ring current (resulting from the loop of pi electrons in the six-membered ring) leads to an induced magnetic field that reinforces the external magnetic field in the vicinity of the aromatic protons; thus these protons, which feel a greater effective field than that applied, come into resonance at lower field (7-8 ppm) than for most other protons:

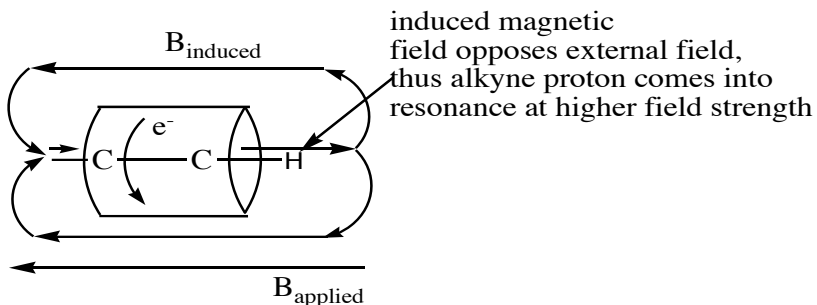


In an alkene, a similar motion of electrons induces a magnetic field which reinforces the applied field, resulting in a deshielding effect, with resonances at 5-6 ppm. Aldehyde protons experience not only the reinforced magnetic field from the nearby pi bond, but also the inductive electron-withdrawing effect of the electronegative oxygen atom. This additive deshielding brings aldehyde protons into resonance at 9-10 ppm.



Additive effect: magnetic field reinforcement and inductive electron-withdrawing effect of oxygen increase deshielding in aldehydes

Acetylenic protons are typically observed at chemical shifts of 2.5 ppm and seem to be shielded relative to alkene protons, aromatic protons, and aldehyde protons. The reason is that since alkynes have a cylinder of electron density surrounding the internuclear axis, the induced magnetic field lines oppose the external applied field, causing these protons to come into resonance at a higher field than alkene and aromatic protons:

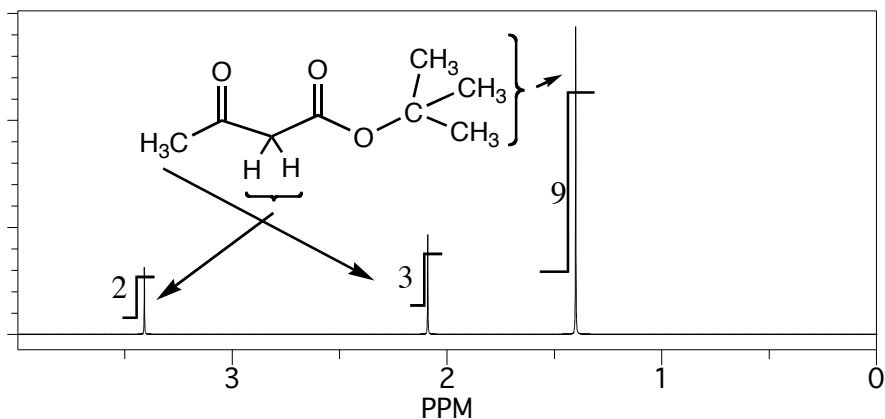
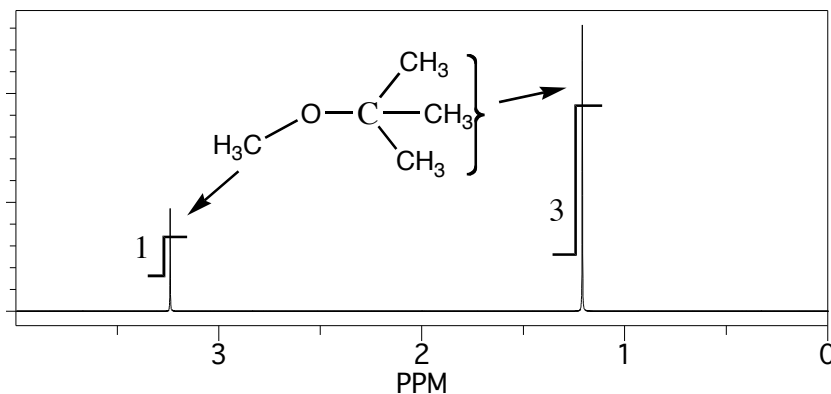


OH and NH chemical shifts vary based on concentration. Higher concentrations of compound containing these functional groups have a greater degree of hydrogen bonding, which deshields the protons even further, causing them to come into resonance at lower field strengths. An extreme case is the carboxylic acid proton, which is strongly deshielded due to the presence of the hydrogen-bonded carboxylic acid dimer structure.

IV. Number of signals and area under peak.

The number of different signals observed in an NMR spectrum indicates the number of different kinds of protons present in the molecule, and the area under the peak, which is indicated by the height of a printed integral over the peak, represents the number of protons per each resonance.

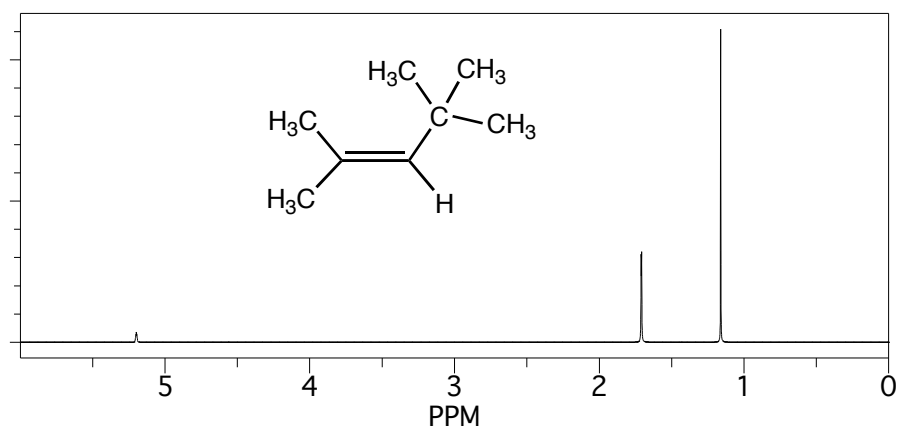
Examples:



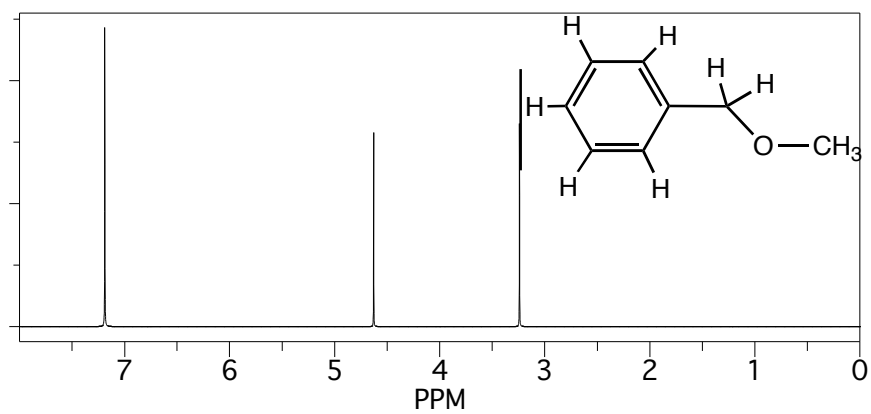
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Additional Problems for practice.
Assign the resonances in the following spectra:

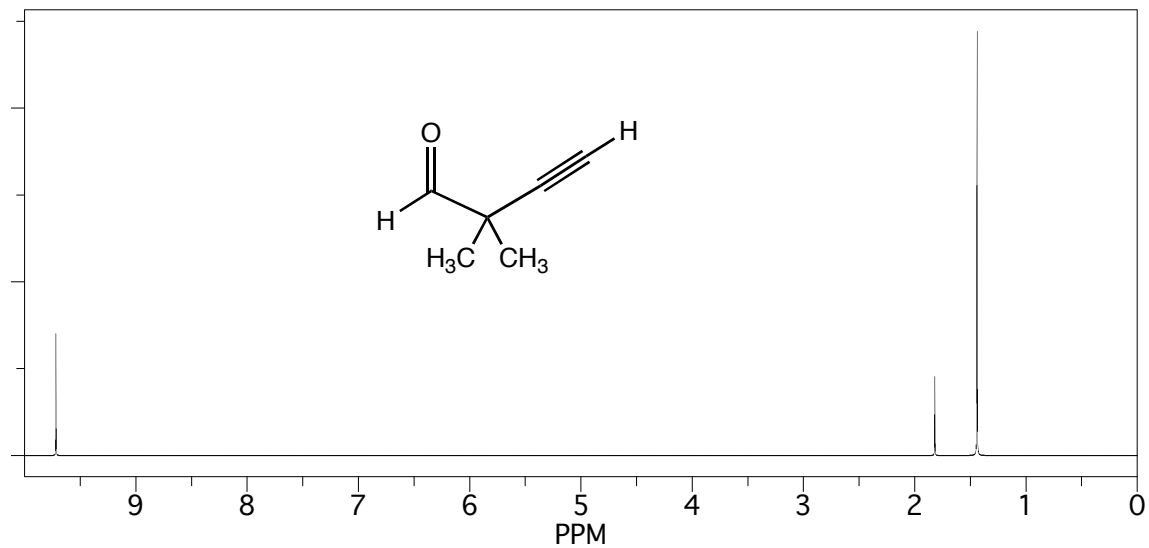
a.



b.



c.



d.

