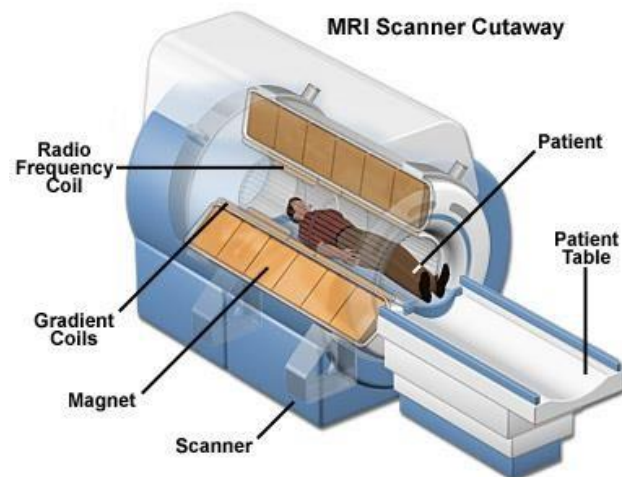
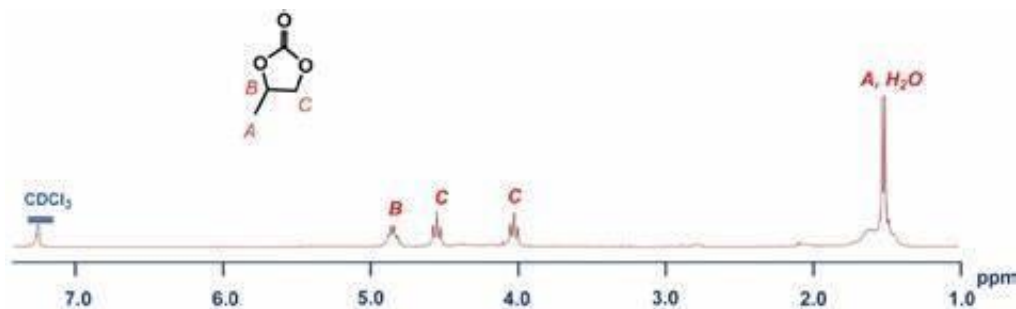


BASIC NMR SPECTROSCOPY

Faculty of Science/Department of Chemistry

4th 2021



INTRODUCTION TO NMR SPECTROSCOPY

- **Nuclear Magnetic Resonance (NMR)** spectroscopy may be the most powerful method of gaining structural information about organic compounds
- **NMR** involves an interaction between electromagnetic radiation (light) and the **nucleus** of an atom
 - We will focus on C and H nuclei for analysis of organic compounds, for obvious reasons
 - The structure (connectivity) of a molecule affects how the radiation interacts with each nucleus in the molecule

INTRODUCTION TO NMR SPECTROSCOPY

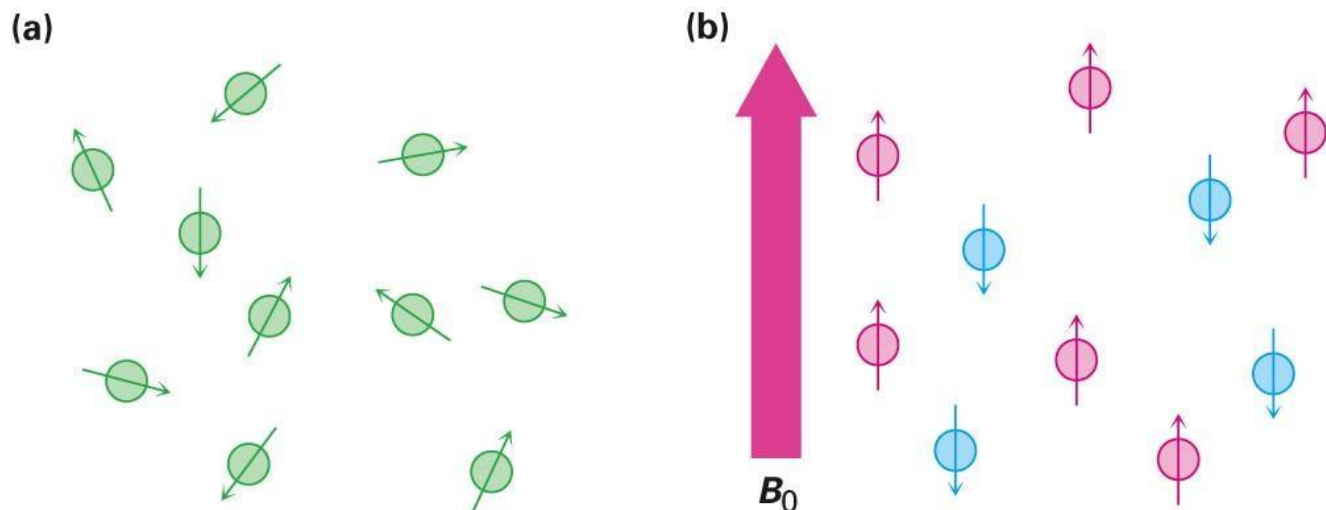
Many atomic nuclei behave as if they spin on an axis of rotation

- Nuclei are positively charged
- These spinning nuclei generate tiny magnetic fields
- Tiny magnets interact with an external magnetic field, denoted B_0
- Proton (^1H) and carbon (^{13}C) are the most important nuclear spins to organic chemists

INTRODUCTION TO NMR SPECTROSCOPY

Nuclear spins are oriented **randomly** in the absence (a) of an external magnetic field but have a specific orientation in the presence (b) of an external field, B_0

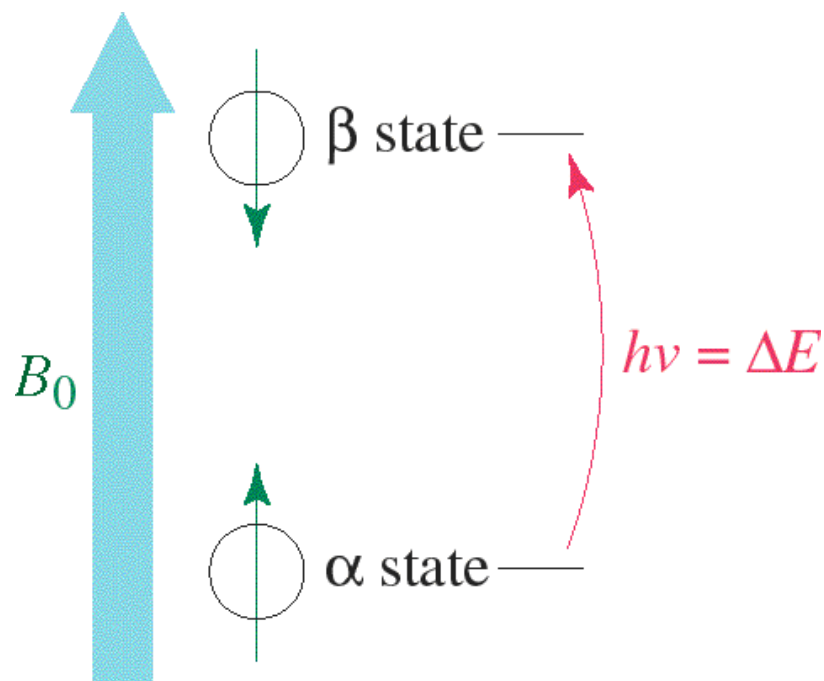
- Some nuclear spins are aligned **parallel** to the external field
 - Lower energy orientation
 - More likely
- Some nuclear spins are aligned **antiparallel** to the external field
 - Higher energy orientation
 - Less likely



Two Energy States

The magnetic fields of the spinning nuclei will align either *with* the external field, or *against* the field.

A photon with the right amount of energy can be absorbed and cause the spinning proton to flip.



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INTRODUCTION TO NMR SPECTROSCOPY

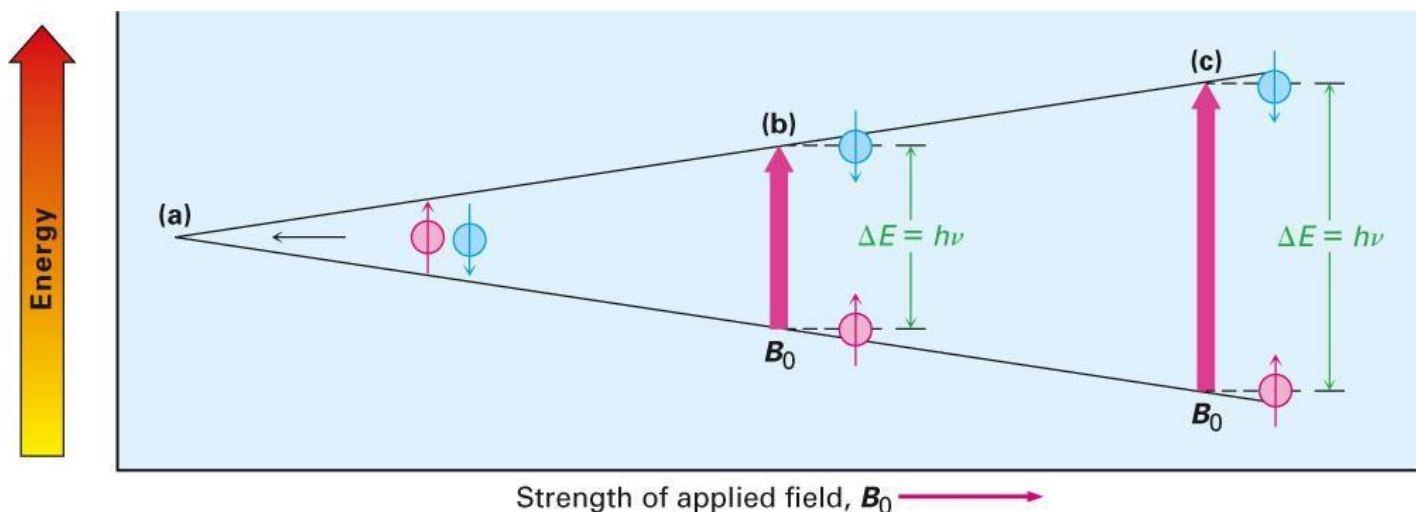
When nuclei that are aligned parallel with an external magnetic field are irradiated with the proper frequency of electromagnetic radiation the energy is absorbed and the nuclei “spin-flips” to the higher-energy antiparallel alignment

- Nuclei that undergo “spin-flips” in response to applied radiation are said to be in resonance with the applied radiation
- *nuclear magnetic resonance*
- Frequency necessary for resonance depends on strength of external field and the identity of the nuclei

INTRODUCTION TO NMR SPECTROSCOPY

The energy difference ΔE between nuclear spin states depends on the strength of the applied magnetic field

- Absorption of energy with frequency ν converts a nucleus from a lower to a higher spin state
 - $\Delta E = 8.0 \times 10^{-5}$ kJ/mol for magnetic field strength of 4.7 T a
 - For field strength of 4.7 T a radiofrequency (rf) of $\nu = 200$ MHz is required to bring ^1H nuclei into resonance
 - For a field strength of 4.7 T a radiofrequency (rf) of $\nu = 50$ MHz is required to bring ^{13}C nuclei into resonance



INTRODUCTION TO NMR SPECTROSCOPY

Many nuclei exhibit NMR phenomenon

- All nuclei with odd number of protons
- All nuclei with odd number of neutrons
- Nuclei with even numbers of both protons and neutrons do not exhibit NMR phenomenon

TABLE 11.1

The NMR Behavior of Some Common Nuclei

Magnetic nuclei	Nonmagnetic nuclei
^1H	^{12}C
^{13}C	^{16}O
^2H	^{32}S
^{14}N	
^{19}F	
^{31}P	

INTRODUCTION TO NMR SPECTROSCOPY

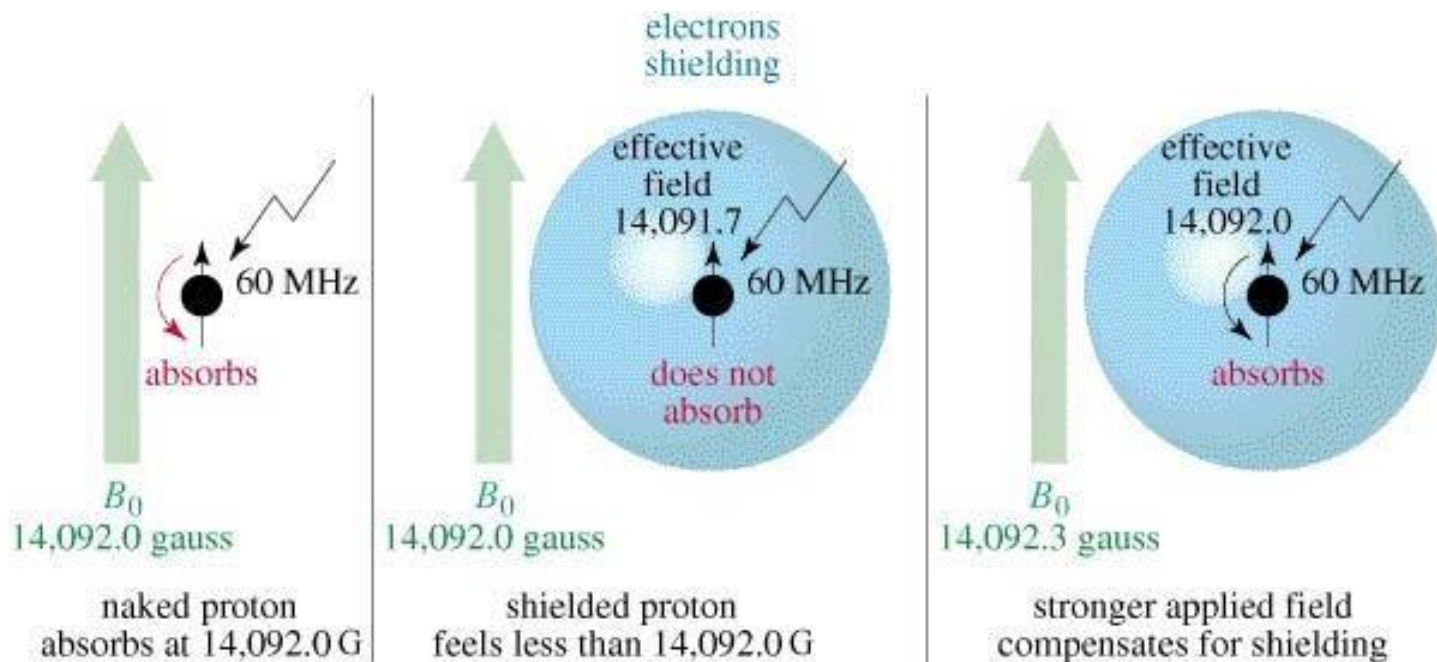
The absorption frequency is not the same for all ^1H and ^{13}C nuclei

- Nuclei in molecules are surrounded by electrons
- Electrons set up tiny local magnetic fields that act in opposition to the applied field, **shielding** the nucleus from the full effect of the external magnetic field
- The *effective* field actually felt by the nucleus is the applied field reduced by the local shielding effects

$$B_{\text{effective}} = B_{\text{applied}} - B_{\text{local}}$$

Shielded Protons

Magnetic field strength must be increased for a shielded proton to flip at the same frequency.



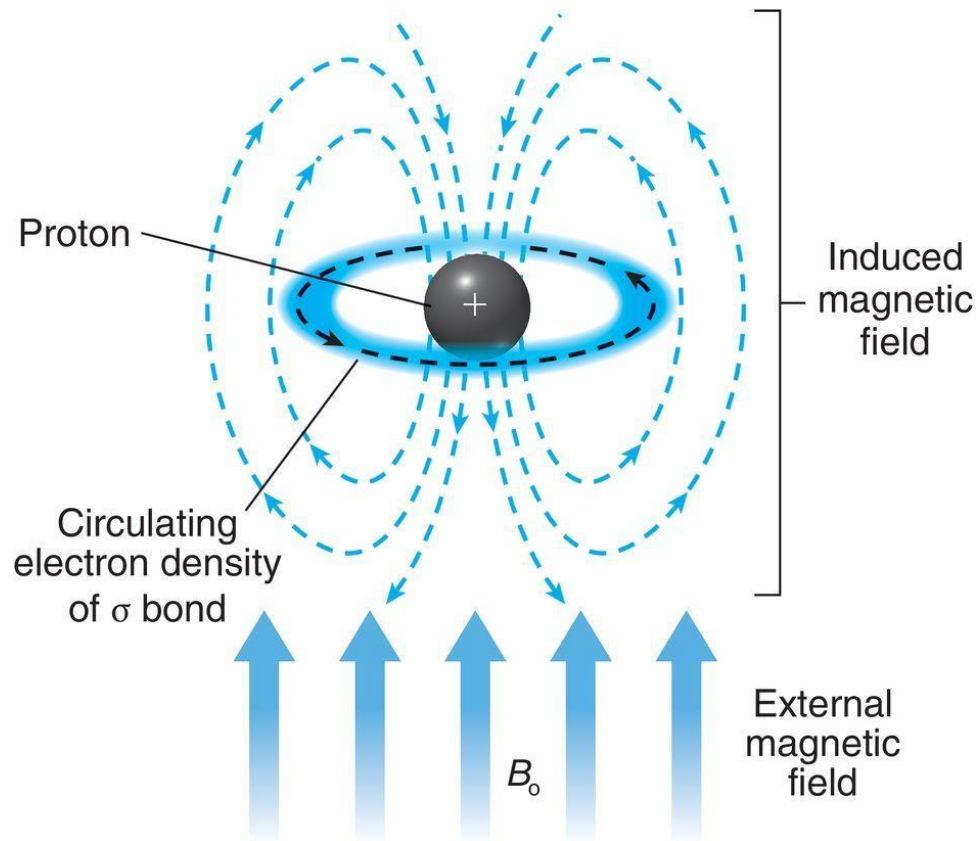
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INTRODUCTION TO NMR SPECTROSCOPY

B_0 causes electrons to circulate, inducing an opposing magnetic field (diamagnetism)

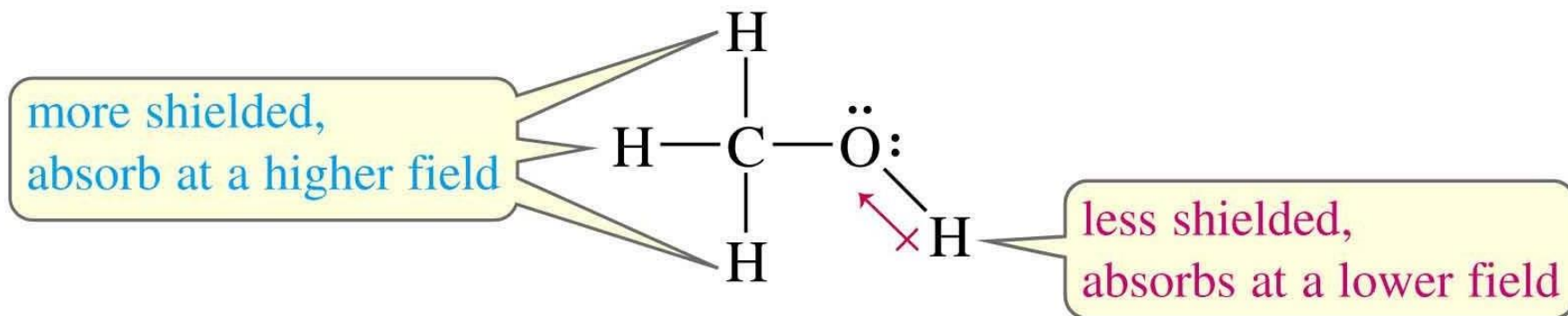
Nuclei then experience **less B_0** , and are said to be **shielded**, requiring less energy to spin flip

Nuclei surrounded by **less electron density** are said to be **deshielded**



Protons in a Molecule

Depending on their chemical environment, protons in a molecule are shielded by different amounts.

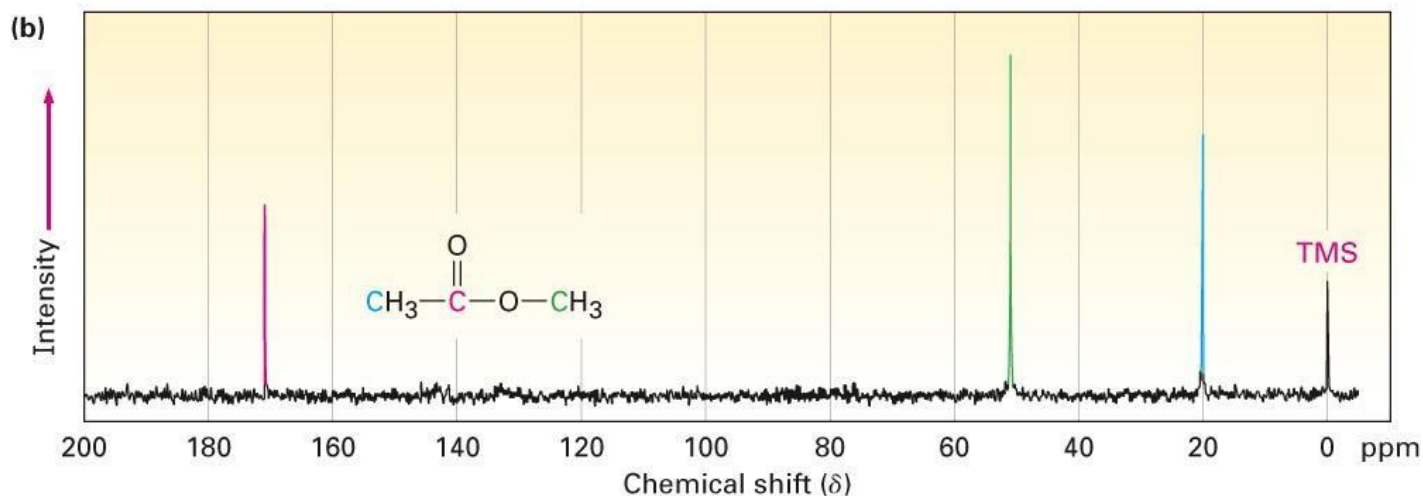
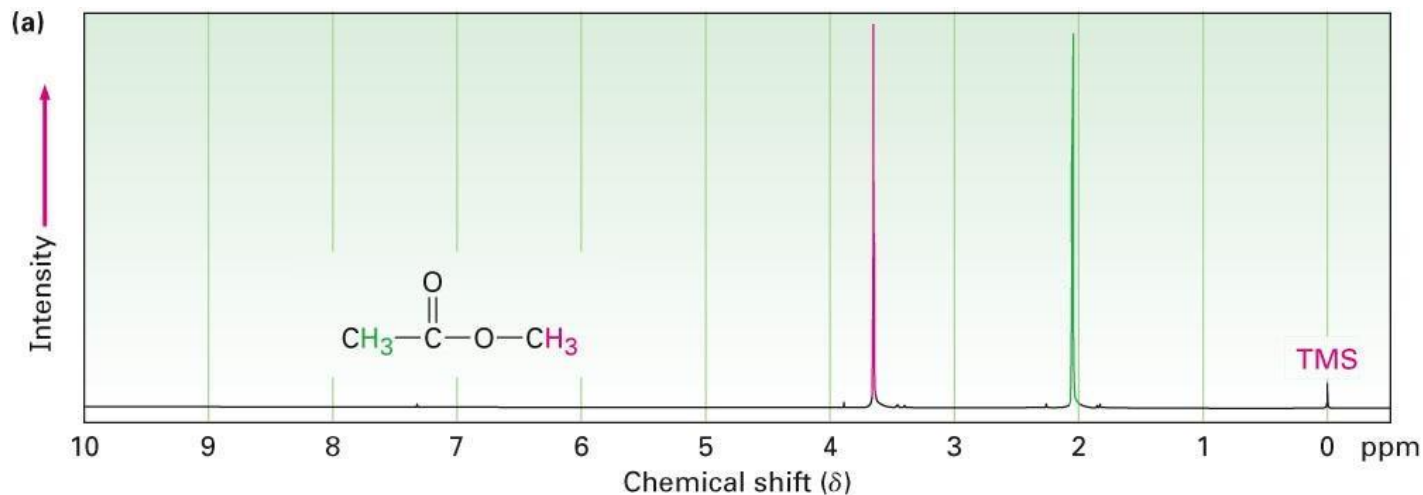


THE NATURE OF NMR ABSORPTIONS

The absorption frequency is not the same for all ^1H and ^{13}C nuclei

- Each chemically distinct nucleus in a molecule has a slightly different electronic environment and consequently a different effective field
- Each chemically distinct ^{13}C or ^1H nucleus in a molecule experiences a different effective field and will exhibit a distinct ^{13}C or ^1H NMR signal

THE NATURE OF NMR ABSORPTIONS

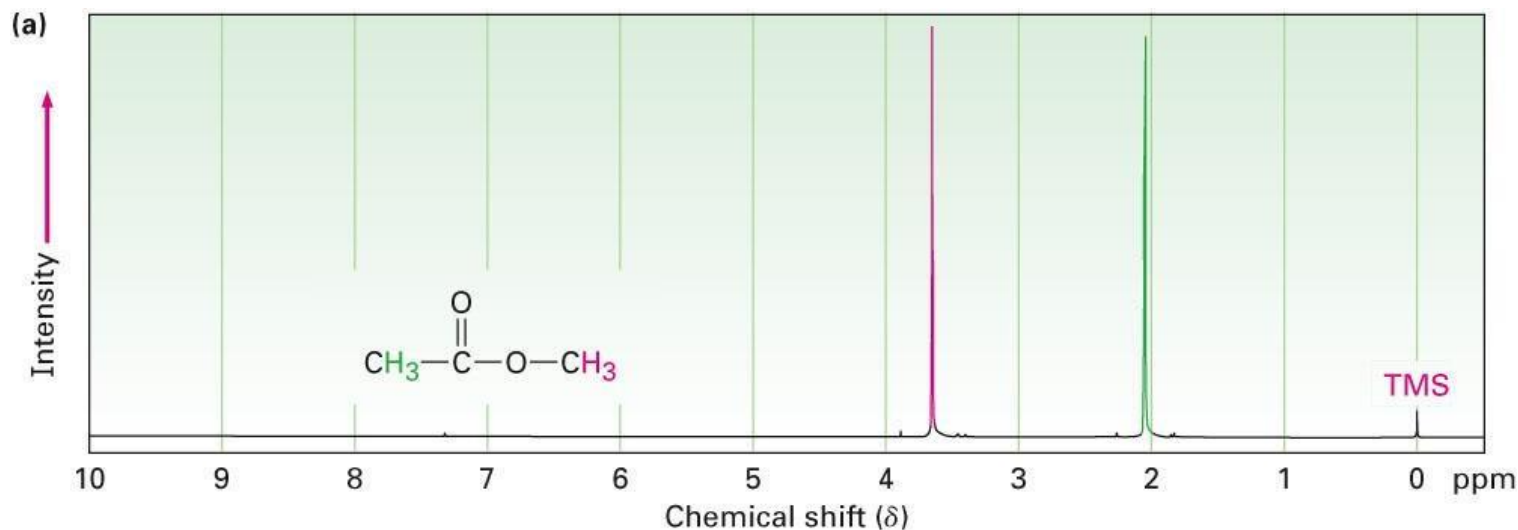


a) ^1H NMR spectrum and (b) ^{13}C NMR spectrum of methyl acetate. Peak labeled “TMS” at far right is for calibration

THE NATURE OF NMR ABSORPTIONS

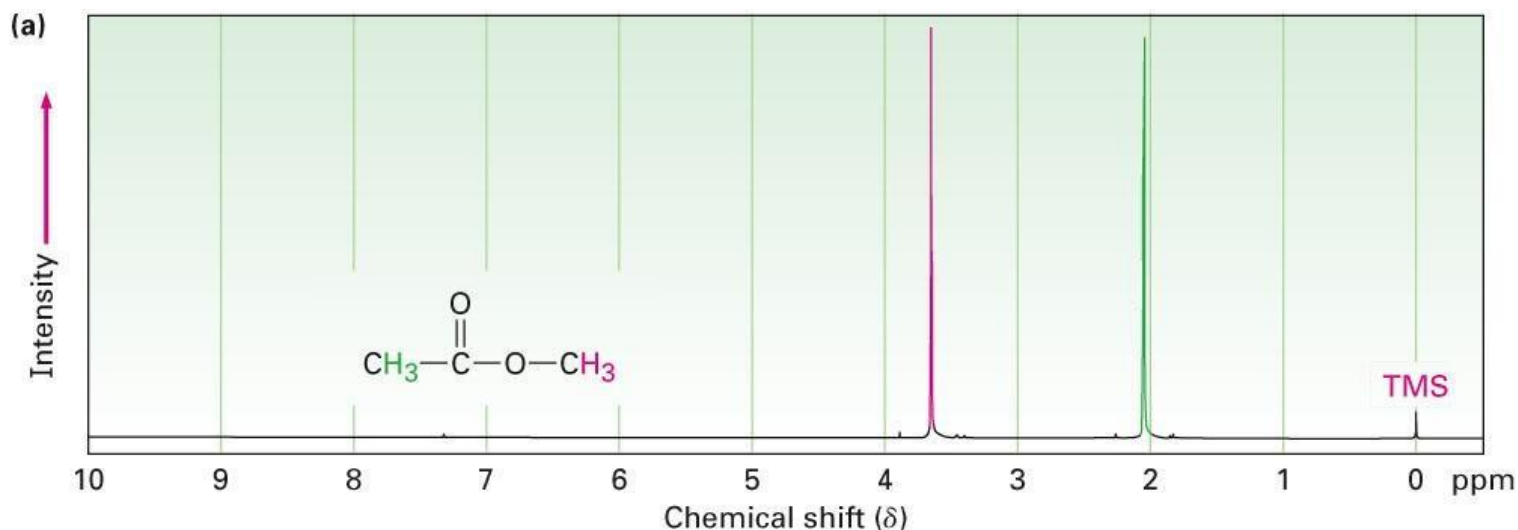
Because the three hydrogens in each methyl group of methyl acetate have the same electronic environment they are shielded to the same extent and are said to be *equivalent*

- *Chemically equivalent nuclei always show the same absorption*
- The three hydrogens in each methyl group have the same ^1H NMR signal



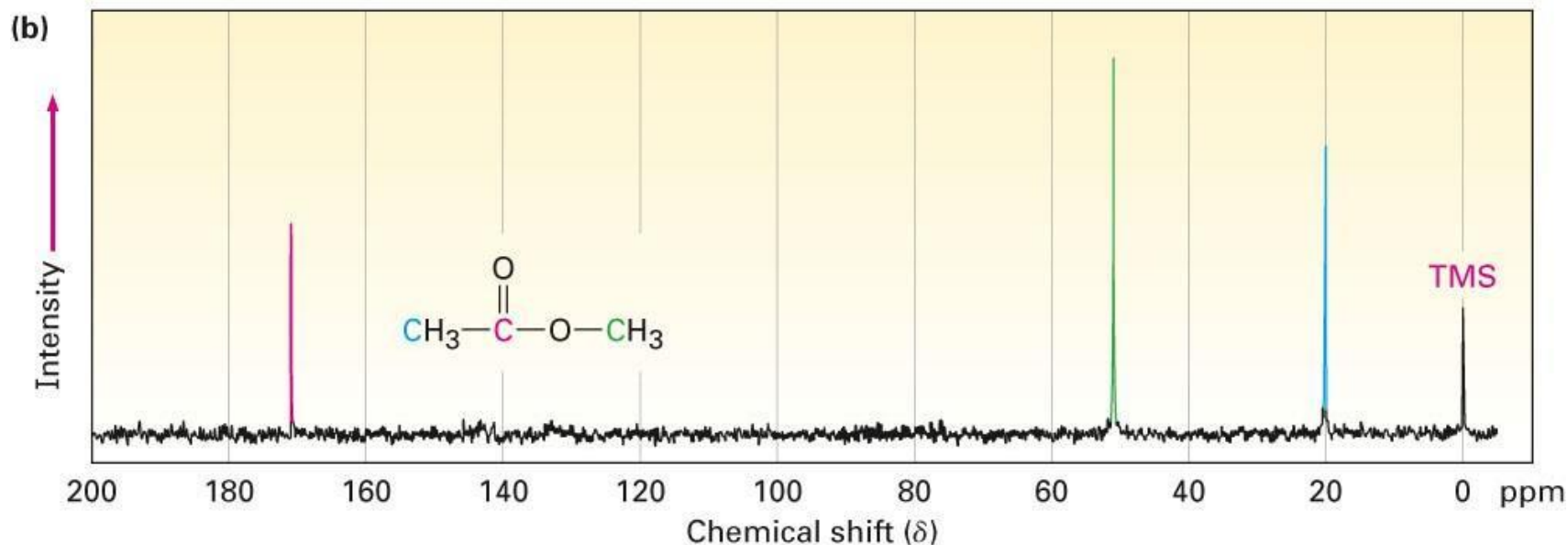
THE NATURE OF NMR ABSORPTIONS

- The two methyl groups of methyl acetate are nonequivalent
 - The two sets of hydrogens absorb at different positions
- When the frequency of rf irradiation is held constant and the applied field strength is varied each nucleus in a molecule comes into resonance at a slightly different field strength, mapping the carbon-hydrogen framework of an organic molecule



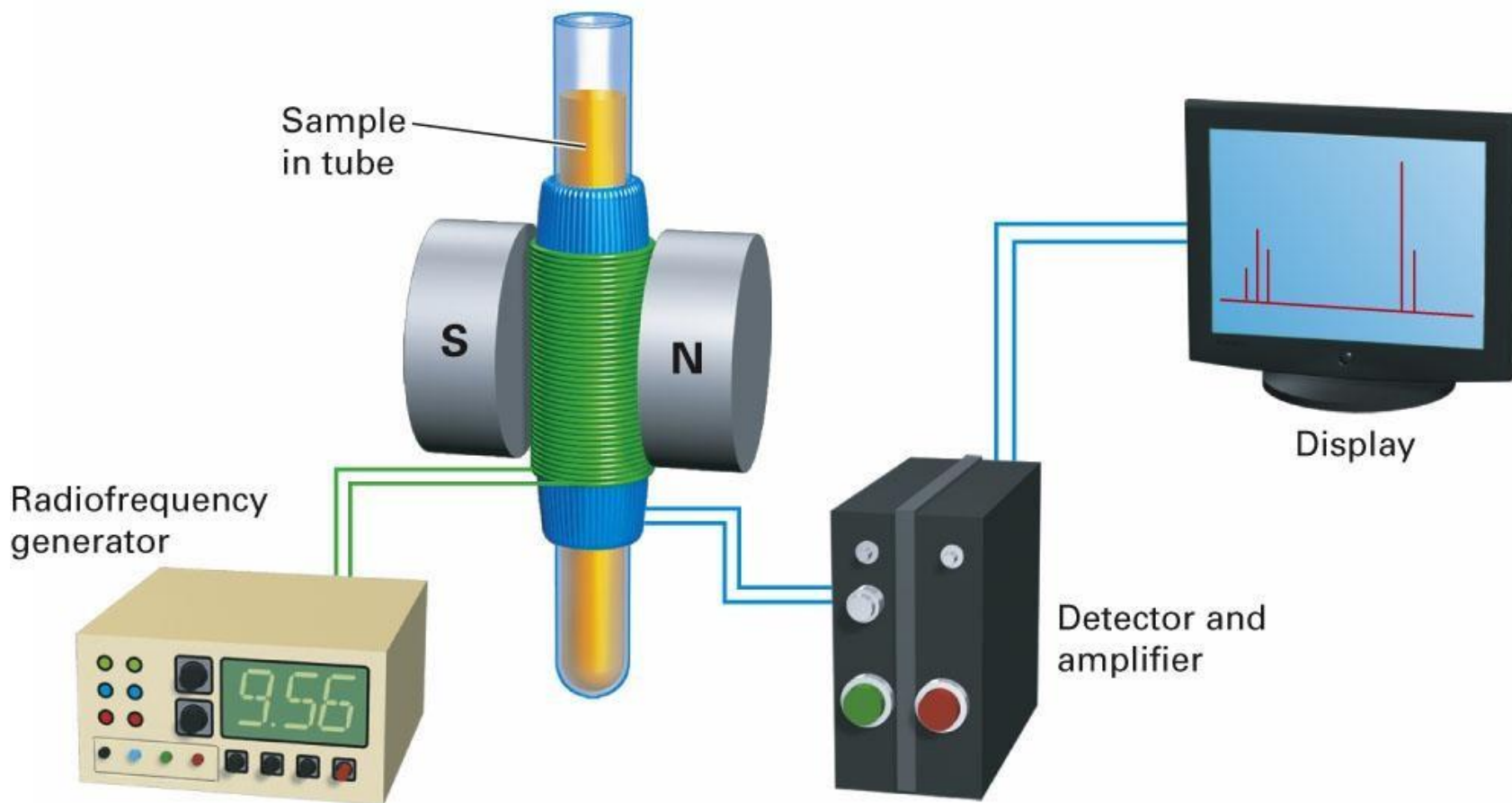
THE NATURE OF NMR ABSORPTIONS

The ^{13}C spectrum of methyl acetate shows three peaks, one for each of the three chemically distinct carbon atoms in the molecule



THE NATURE OF NMR ABSORPTIONS

Schematic operation of a basic NMR spectrometer



300MHz NMR



900MHz NMR

