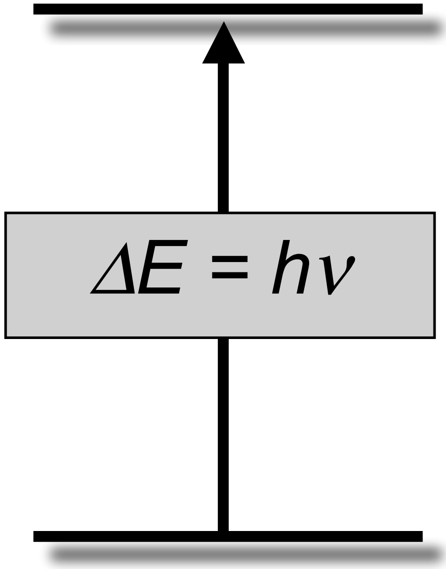
Principles of Molecular Spectroscopy: Electromagnetic Radiation and Molecular structure

Nuclear Magnetic Resonance (NMR)



$\Delta E = h\nu$

Electromagnetic radiation is absorbed when the energy of photon corresponds to difference in energy between two states.

What Kind of States?

electronic	UV-Vis
vibrational	infrared
rotational	microwave
nuclear spin	radiofrequency

NMR is concerned with change in the direction of spin orientation as the result of the absorption of radiofrequency radiation.

The two nuclei that are most useful to organic chemists are:

^{1}H and ^{13}C

both have spin = ±1/2

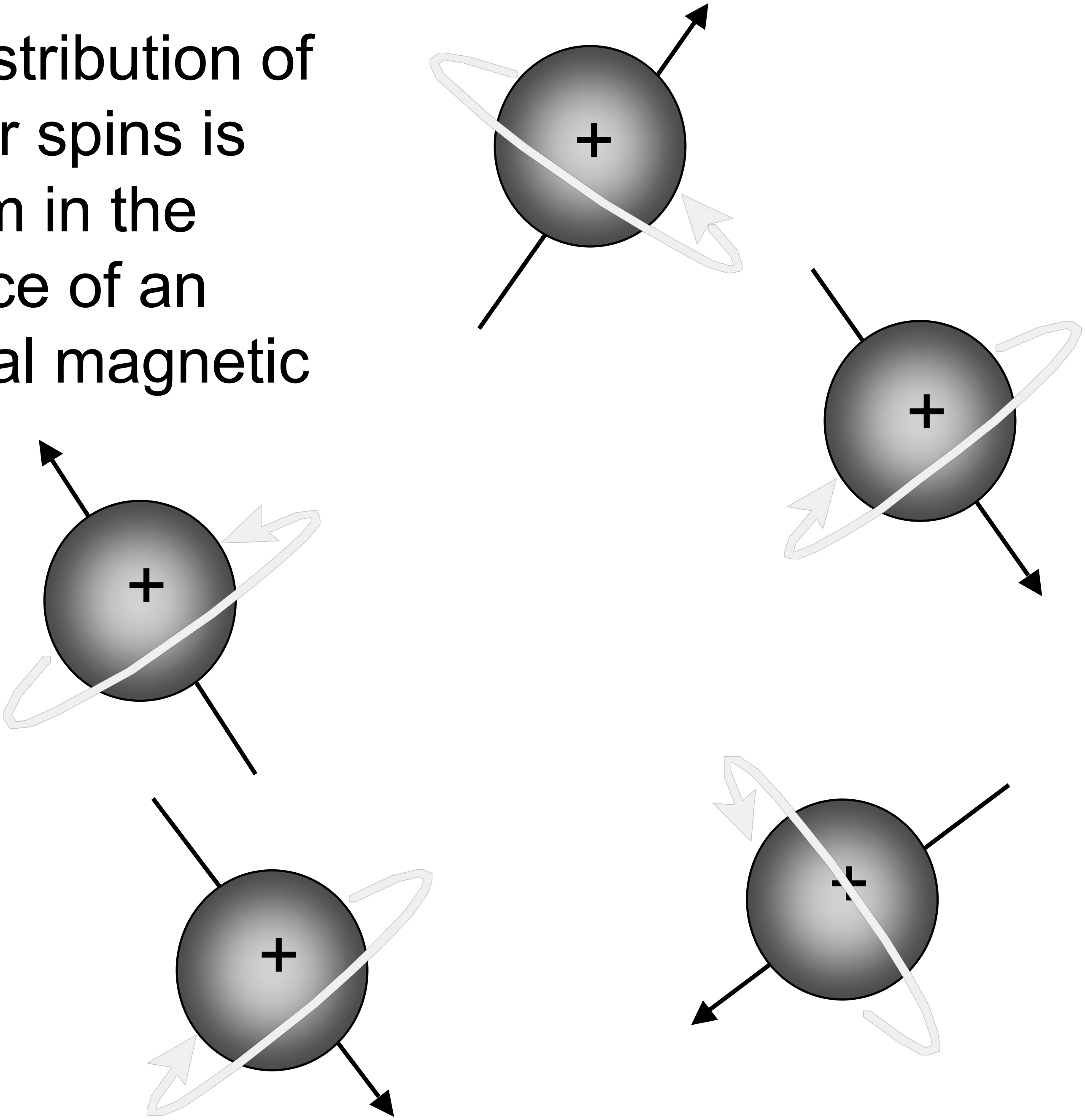
^{1}H is 99% at natural abundance

^{13}C is 1.1% at natural abundance

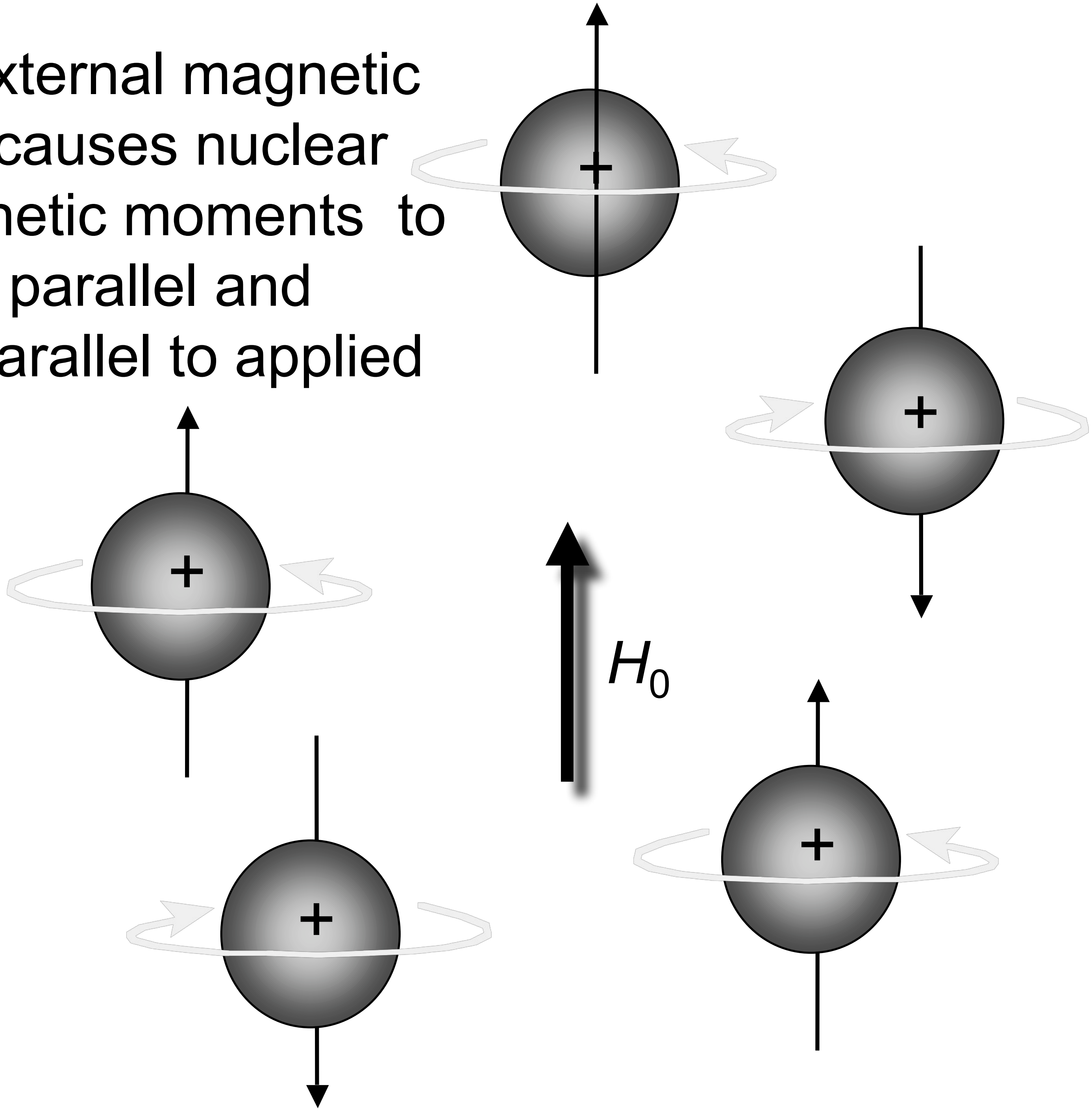
Nuclear Spin

A spinning charge, such as the nucleus of ^1H or ^{13}C, generates a magnetic field. The magnetic field generated by a nucleus of spin +1/2 is opposite in direction from that generated by a nucleus of spin –1/2.

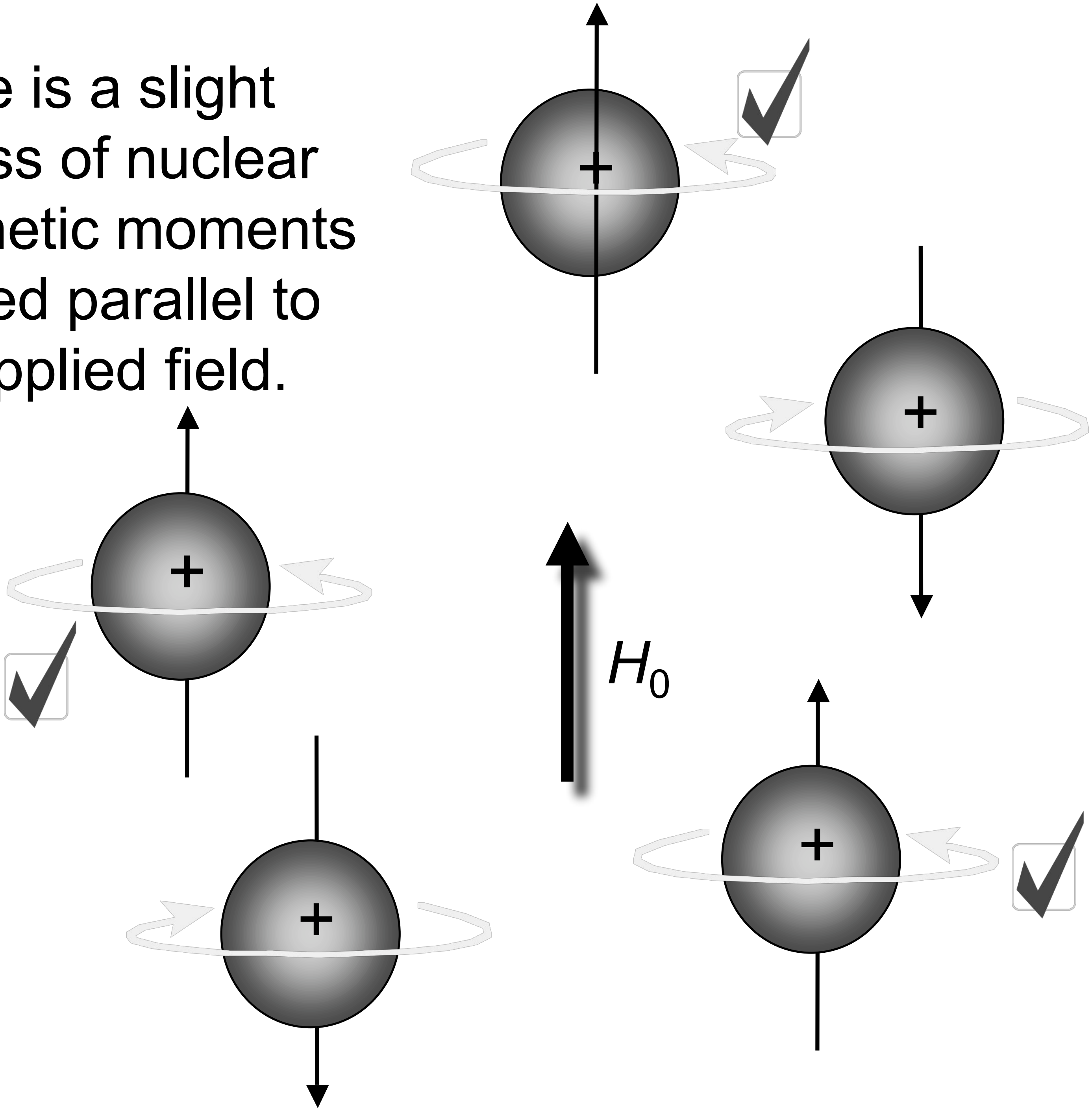
The distribution of nuclear spins is random in the absence of an external magnetic field.



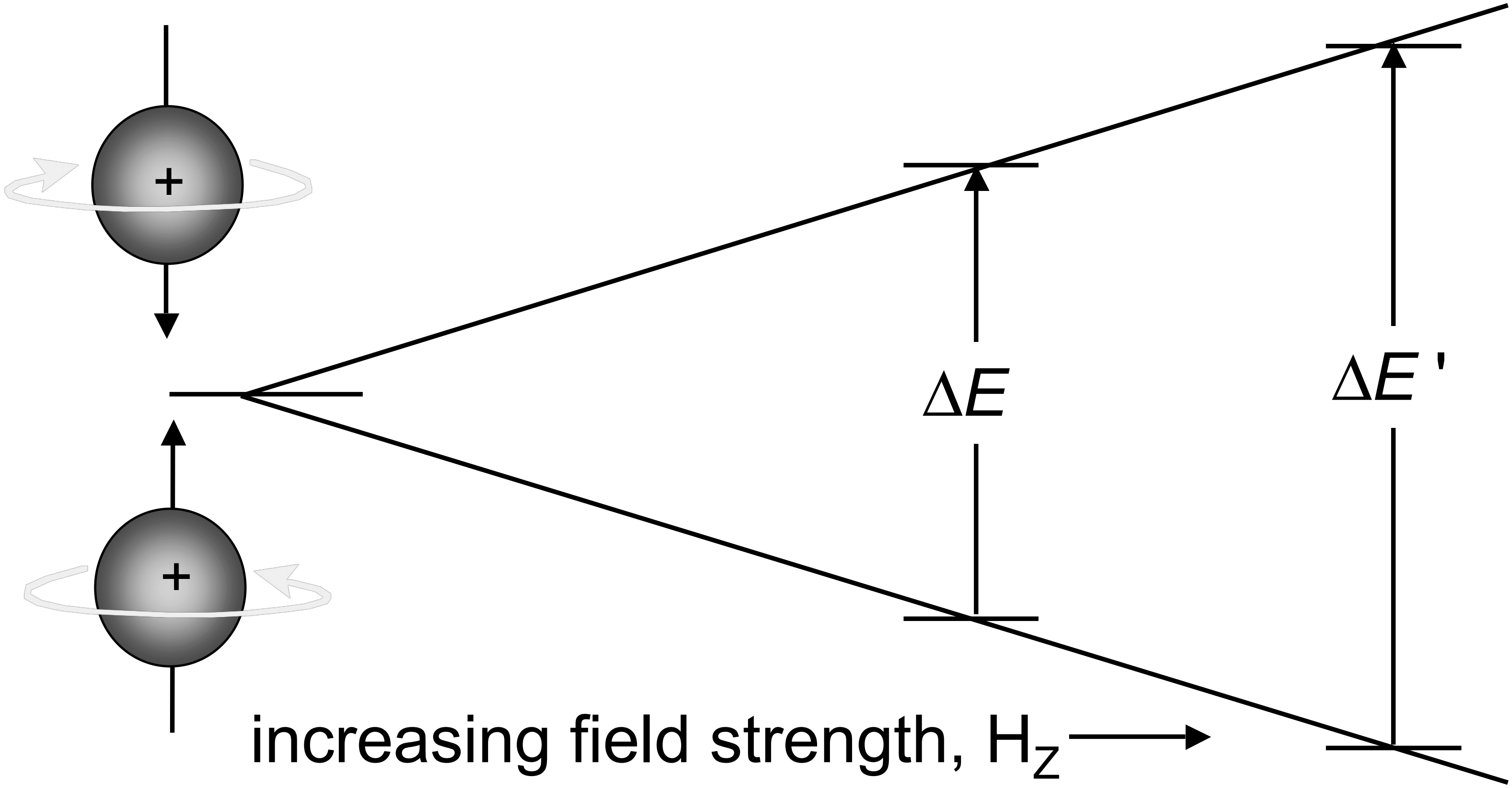
An external magnetic field causes nuclear magnetic moments to align parallel and antiparallel to applied field.



There is a slight excess of nuclear magnetic moments aligned parallel to the applied field.



Energy Differences Between Nuclear Spin States



increasing field strength, H_Z →

no energy difference in absence of magnetic field
proportional to strength of external magnetic field

Some important relationships in NMR

The frequency of absorbed
electromagnetic radiation
is proportional to

the energy difference between
two nuclear spin states
which is proportional to

the applied magnetic field

Some important relationships in NMR

	Units
The frequency (ν) of absorbed electromagnetic radiation is proportional to	Hz (s^{-1})
the energy difference (ΔE) between two nuclear spin states which is proportional to	kJ/mol (kcal/mol)
the applied magnetic field (H_0)	tesla (T)

Some important relationships in NMR

The frequency of absorbed electromagnetic radiation is different for different elements, and for different isotopes of the same element.

For a field strength of $H_0 = 4.7$ T:

^1H absorbs radiation having a frequency of 200 MHz ($200 \times 10^6\ s^{-1}$)

^{13}C absorbs radiation having a frequency of 50.4 MHz ($50.4 \times 10^6\ s^{-1}$)

Compare to $10^{15}\ s^{-1}$ for electrons; $10^{13}\ s^{-1}$ for vibrations

Some important relationships in NMR

The frequency of absorbed electromagnetic radiation for a particular nucleus (such as ^{1}H or ^{13}C) depends on the ***molecular*** environment of the nucleus (the electronic environment).

This is why NMR is such a useful tool for structure determination. The signals of different protons and carbon atoms in a molecule show different signals, just like different functional groups show different signals in the IR.

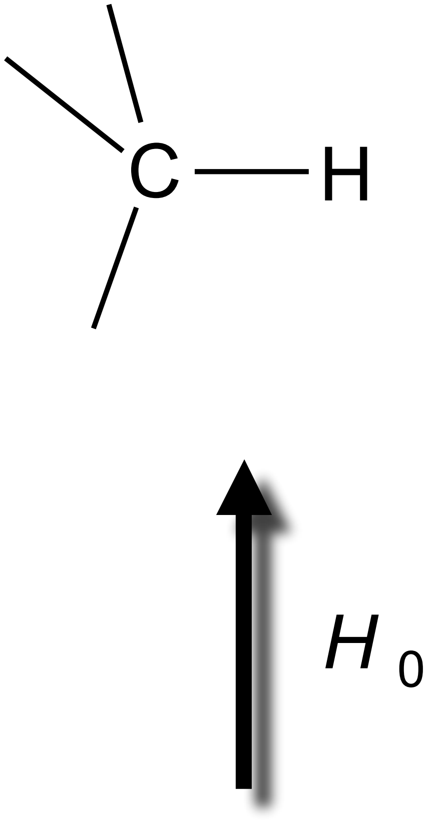
Nuclear Shielding
and
^{1}H Chemical Shifts

What do we mean by "shielding?"

What do we mean by "chemical shift?"

Shielding

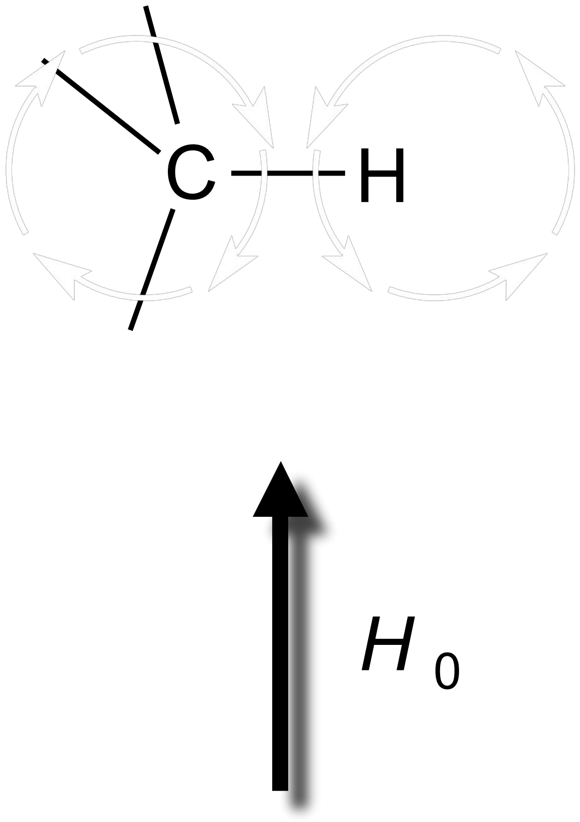
An external magnetic field affects the motion of the electrons in a molecule, inducing a magnetic field within the molecule.



Shielding

An external magnetic field affects the motion of the electrons in a molecule, inducing a magnetic field within the molecule.

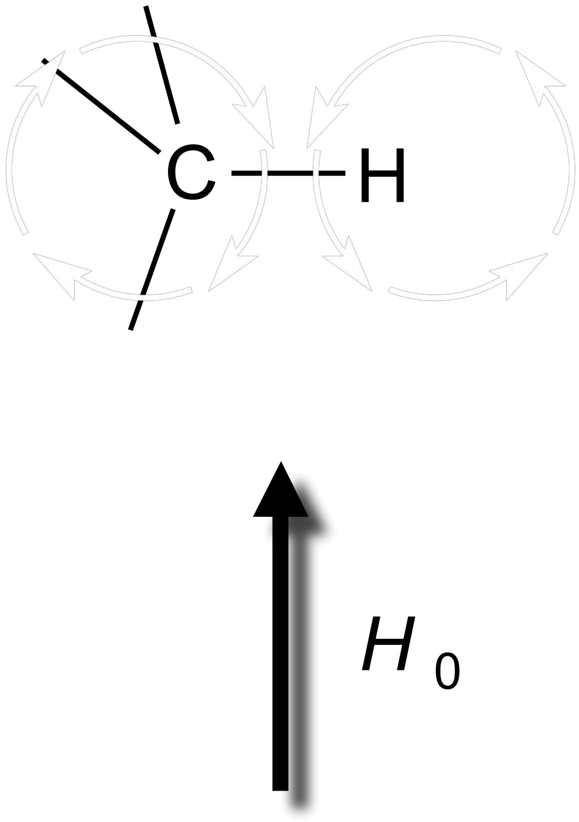
The direction of the induced magnetic field is opposite to that of the applied field.



Shielding

The induced field shields the nuclei (in this case, ^{13}C and ^{1}H) from the applied field.

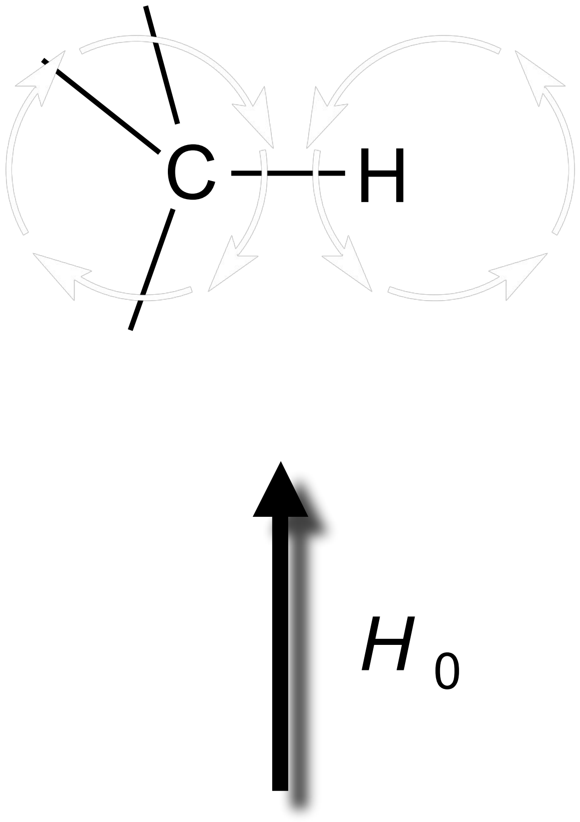
A stronger external field is needed in order for energy difference between spin states to match energy of rf radiation.

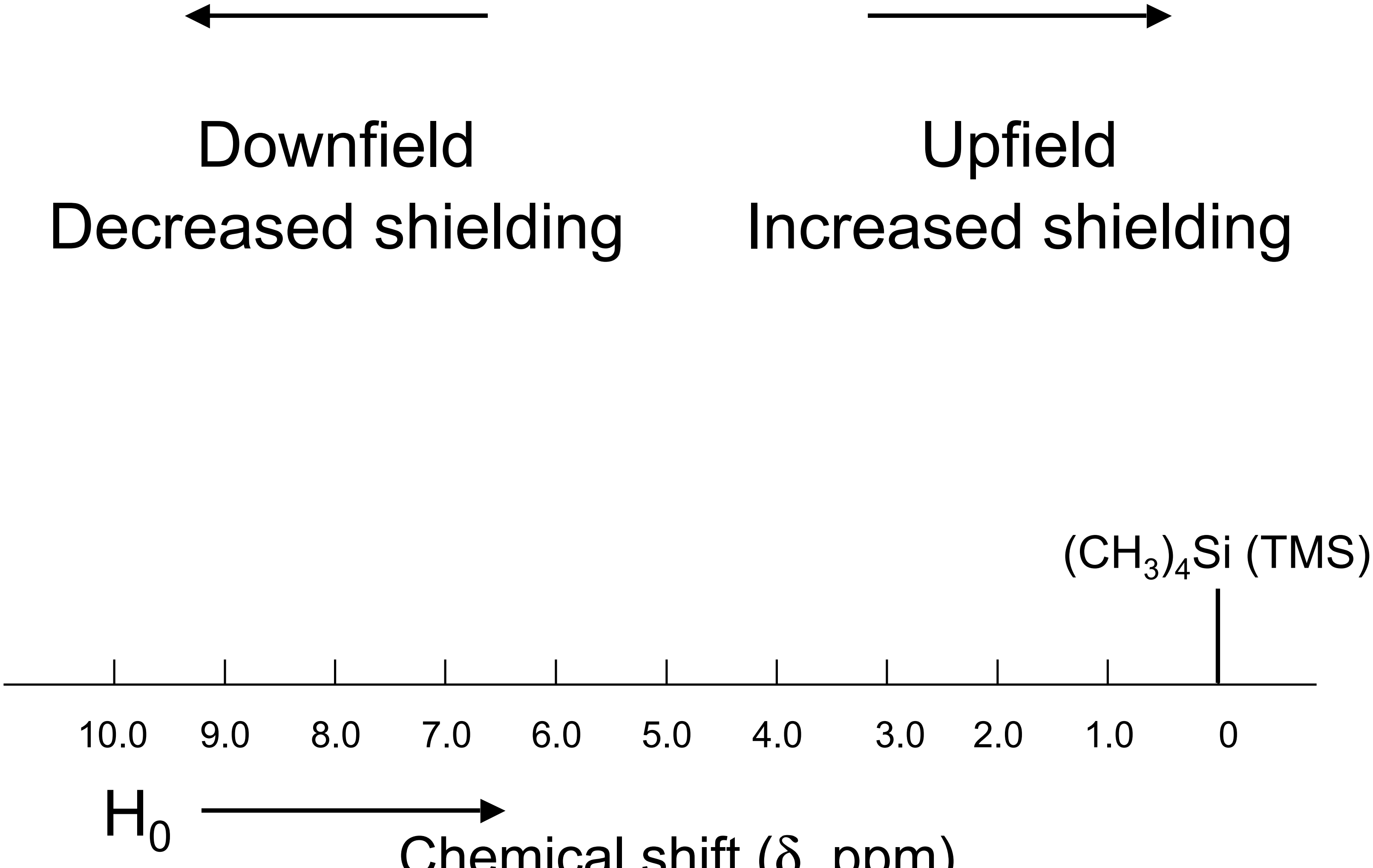


Chemical Shift

Chemical shift is a measure of the degree to which a nucleus in a molecule is shielded.

Protons in different environments are shielded to greater or lesser degrees; they have different chemical shifts.





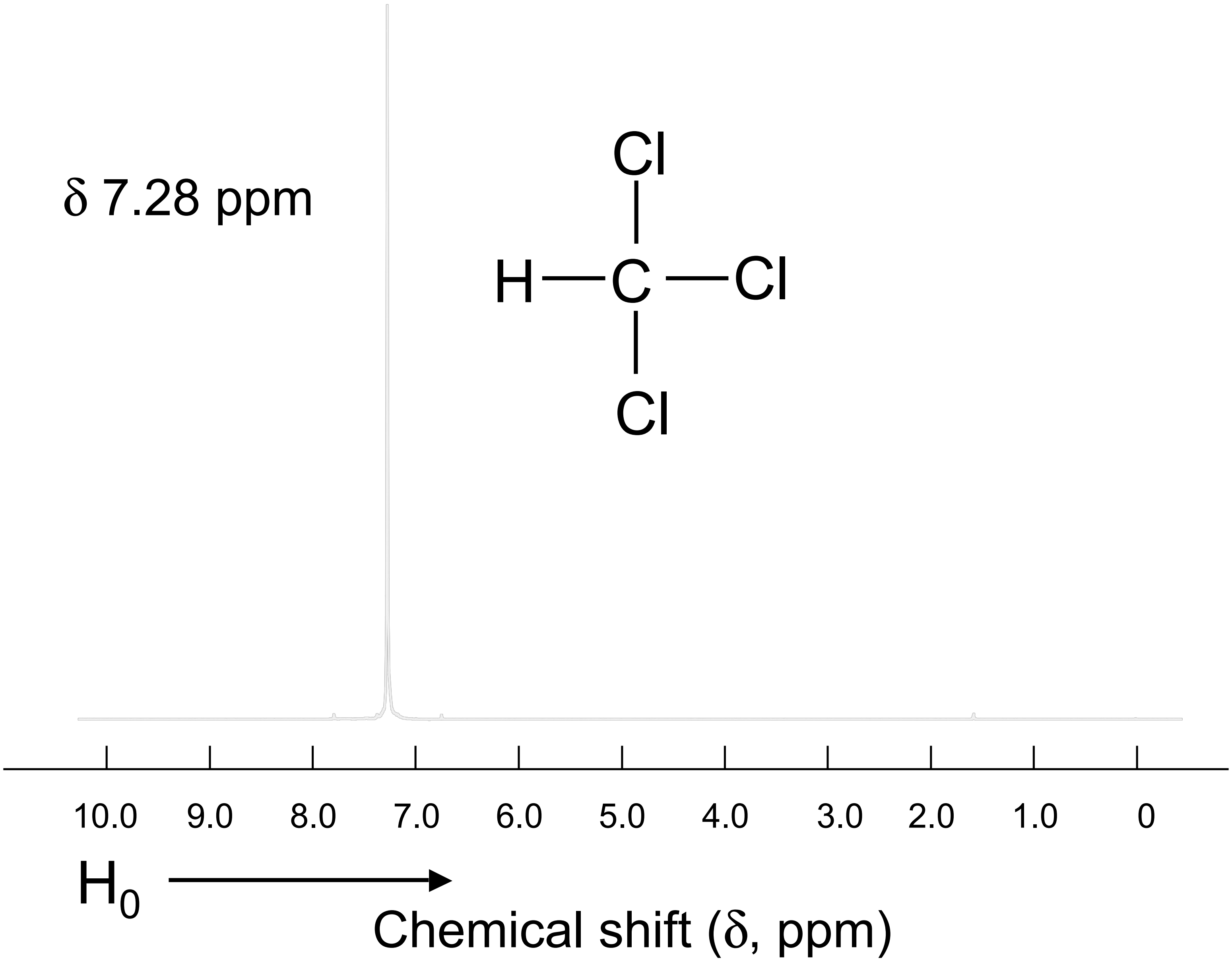
Downfield
Decreased shielding

Upfield
Increased shielding

$(CH_3)_4Si$ (TMS)

H_0

Chemical shift (δ, ppm)
measured relative to TMS

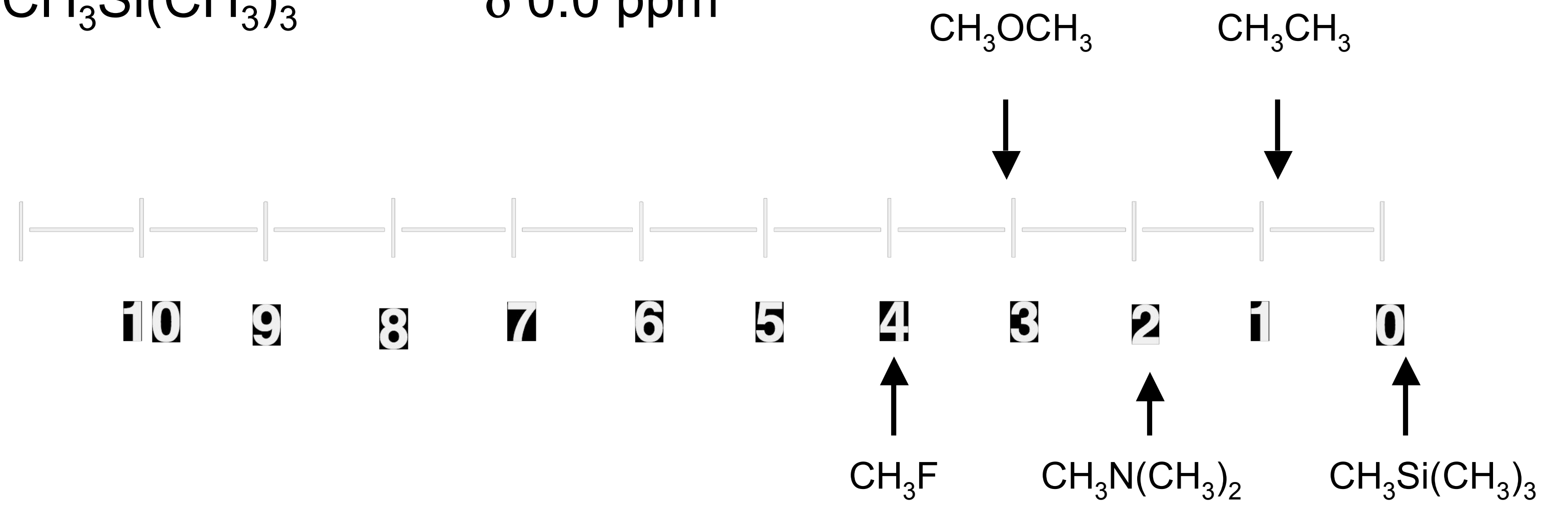

δ 7.28 ppm
Cl
H
C
Cl
Cl
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
H0
Chemical shift (δ, ppm)

Effects of Molecular Structure
on
^{1}H Chemical Shifts

protons in different environments experience different degrees of shielding and have different chemical shifts

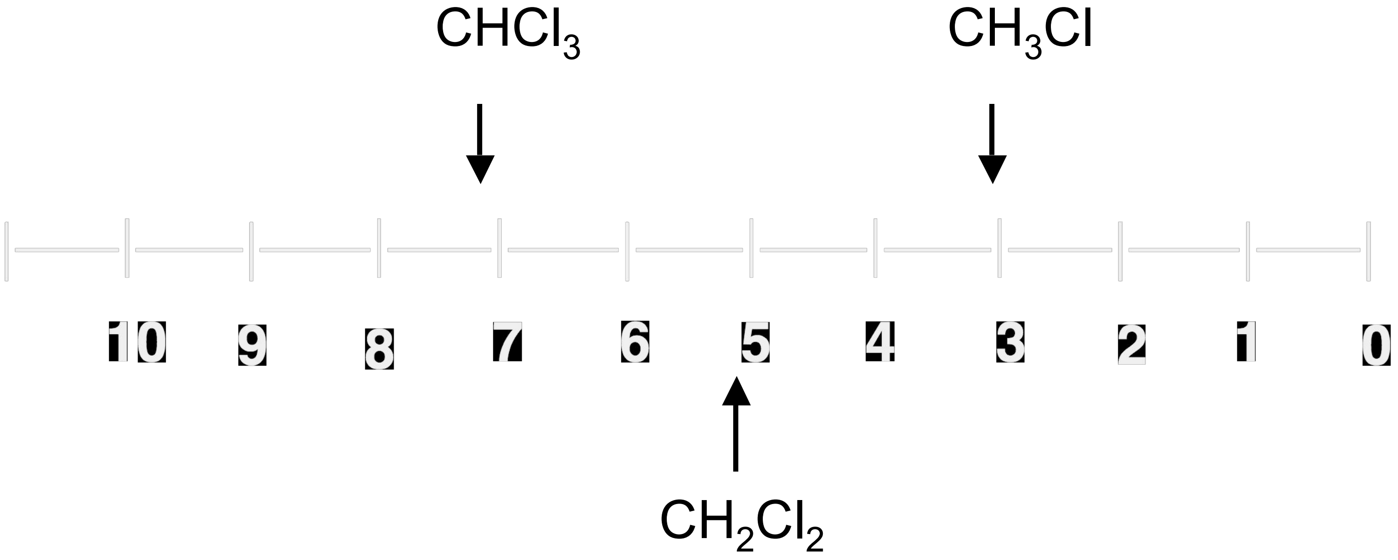
Electronegative substituents decrease the shielding of methyl groups

CH_3F	δ 4.3 ppm
CH_3OCH_3	δ 3.2 ppm
$CH_3N(CH_3)_2$	δ 2.2 ppm
CH_3CH_3	δ 0.9 ppm
$CH_3Si(CH_3)_3$	δ 0.0 ppm

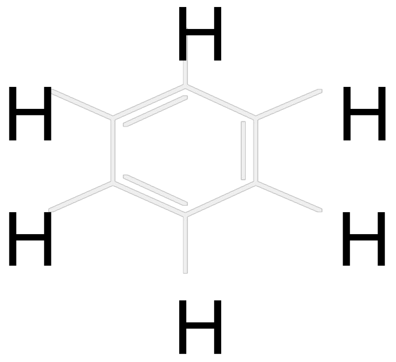


Effect is cumulative

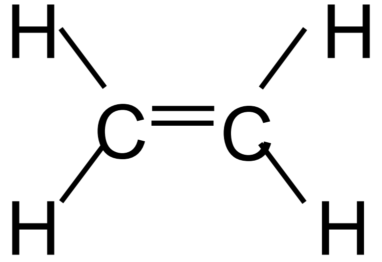
$CHCl_3$	δ 7.3 ppm
CH_2Cl_2	δ 5.3 ppm
CH_3Cl	δ 3.1 ppm



Protons attached to sp^2 hybridized carbon are less shielded than those attached to sp^3 hybridized carbon



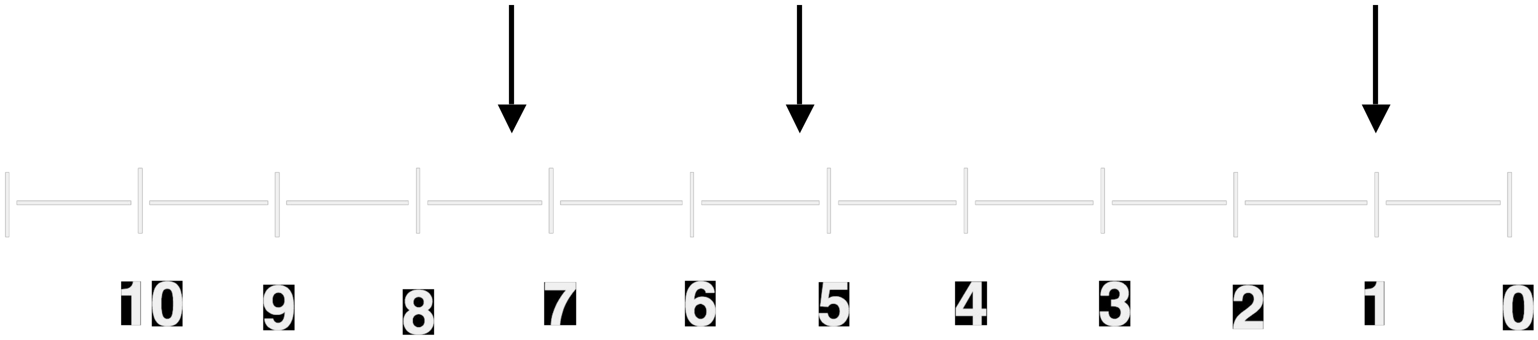
δ 7.3 ppm



δ 5.3 ppm

CH_3CH_3

δ 0.9 ppm



Information contained in an NMR spectrum includes:

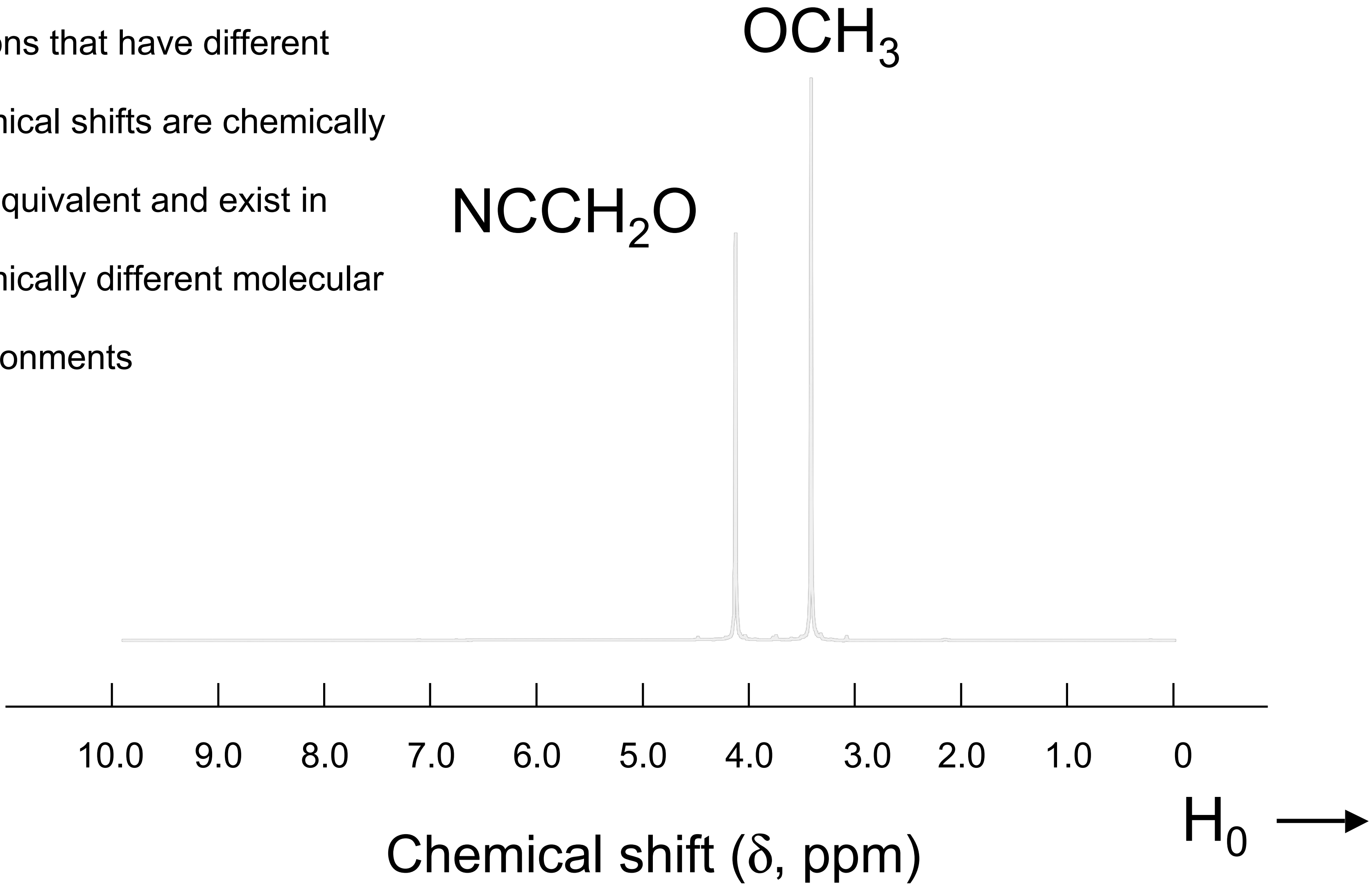
1. number of signals
2. their intensity (as measured by area under peak)
3. splitting pattern (multiplicity)

We shall not consider spin-spin splitting

Number of Signals

$N\equiv CCH_2OCH_3$

protons that have different chemical shifts are chemically nonequivalent and exist in chemically different molecular environments

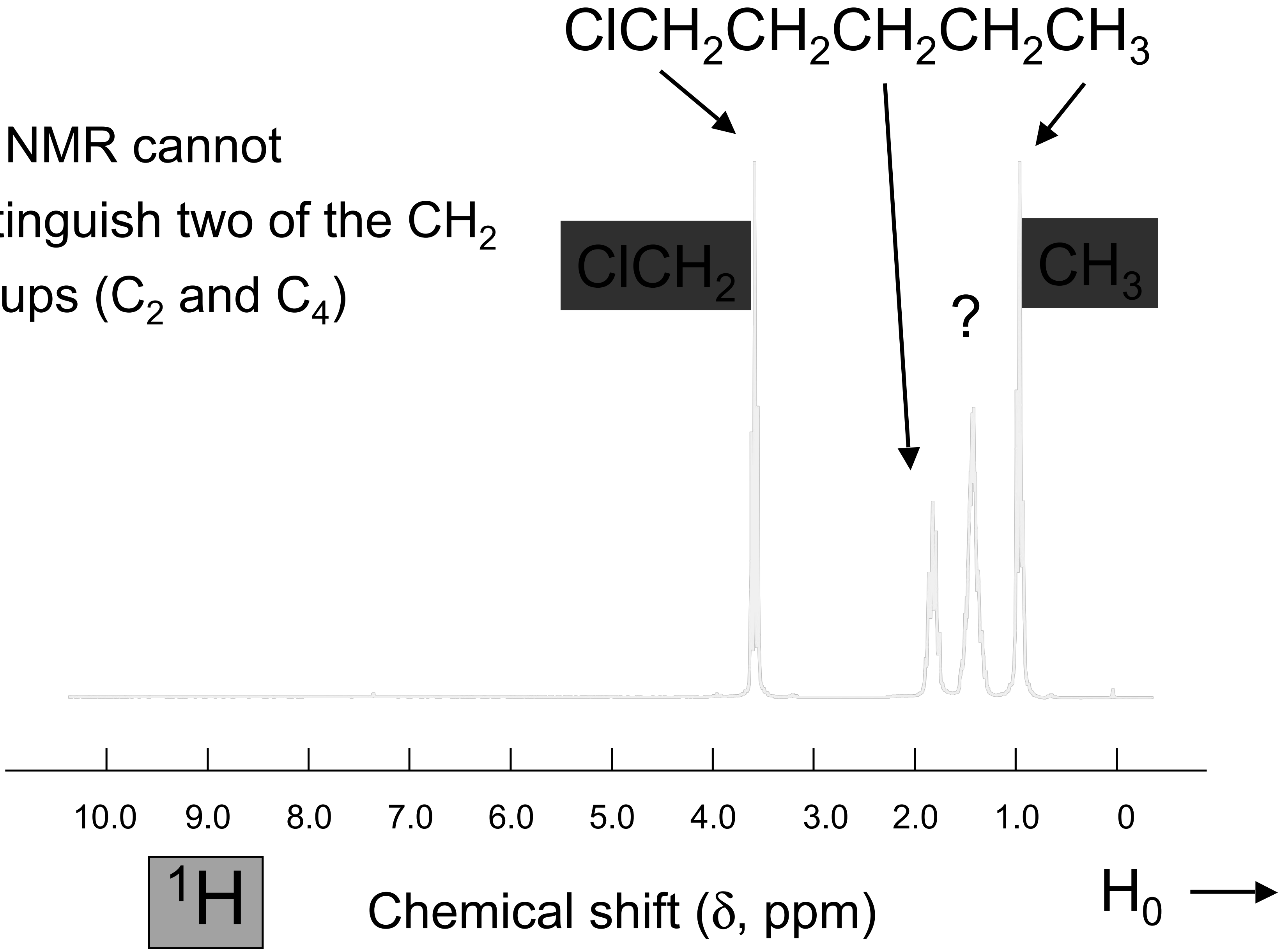


^{1}H and ^{13}C NMR compared:

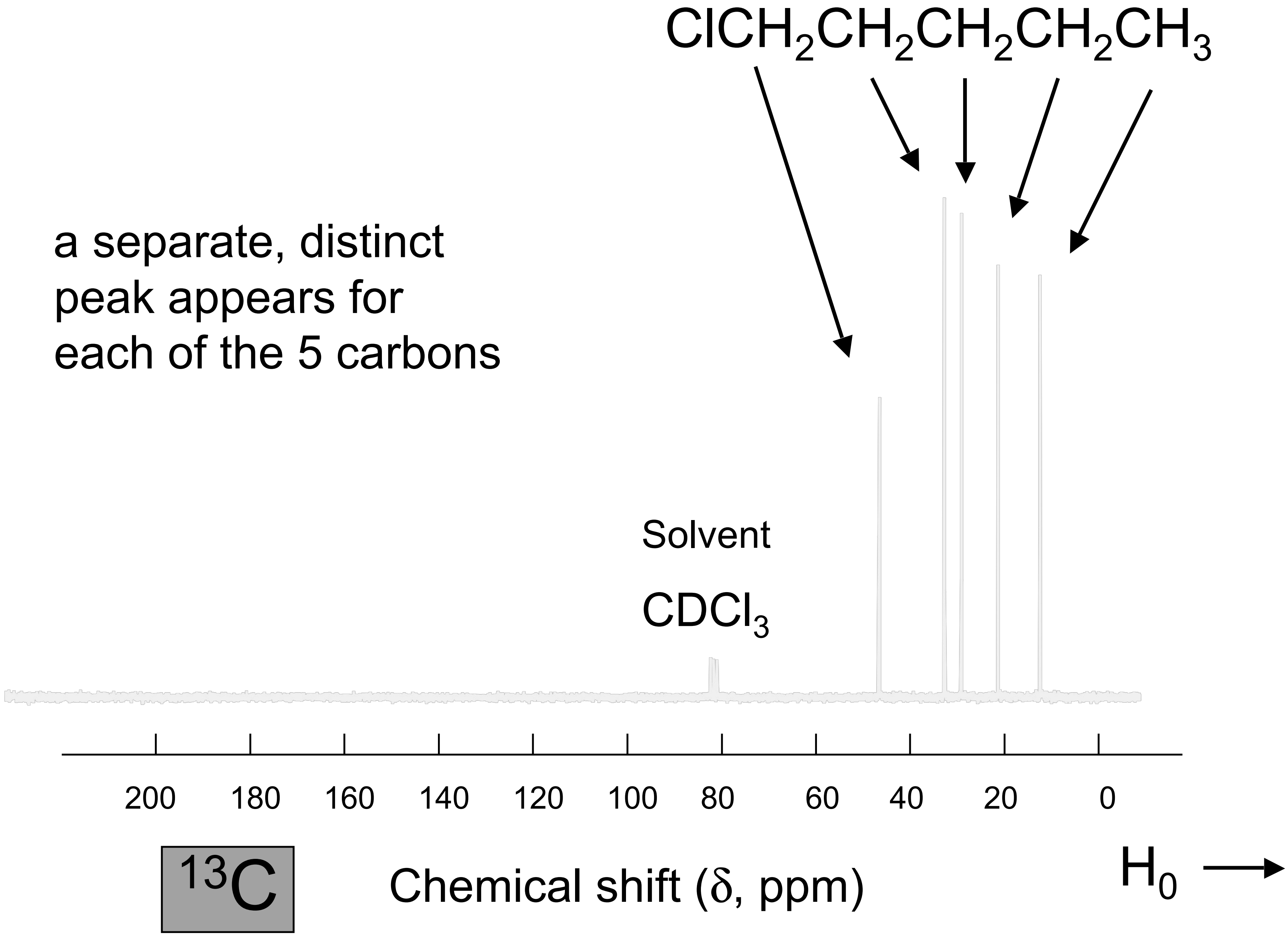
both give us information about the number of chemically nonequivalent nuclei (nonequivalent hydrogens or nonequivalent carbons)

both give us information about the environment of the nuclei (hybridization state, attached atoms, etc.)

1H NMR cannot distinguish two of the CH_2 groups (C_2 and C_4)

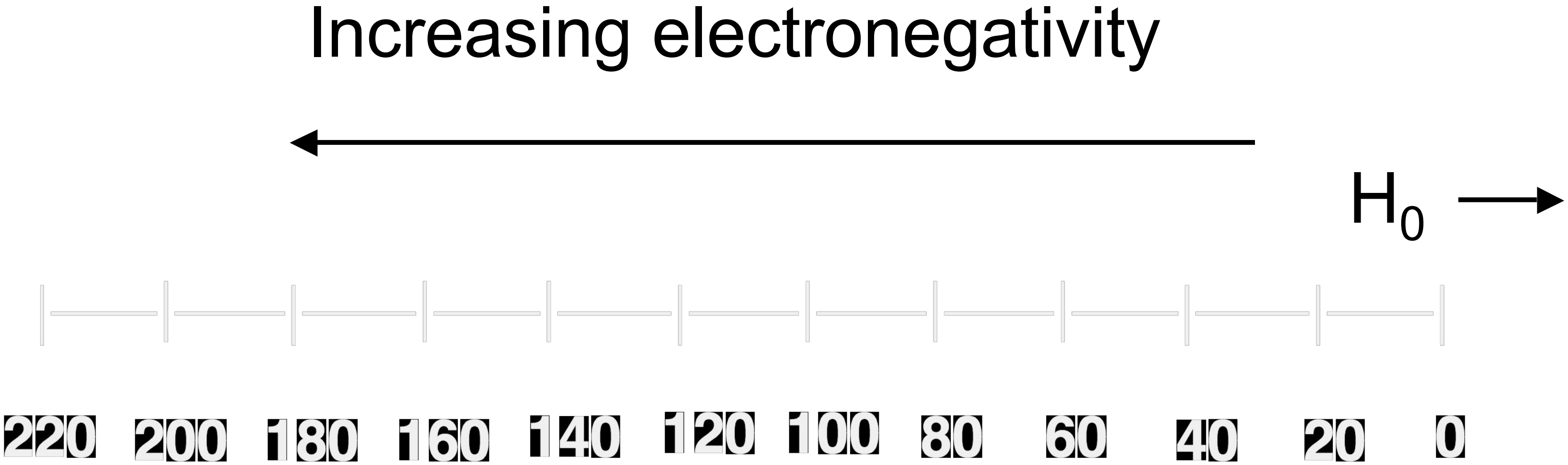


a separate, distinct peak appears for each of the 5 carbons



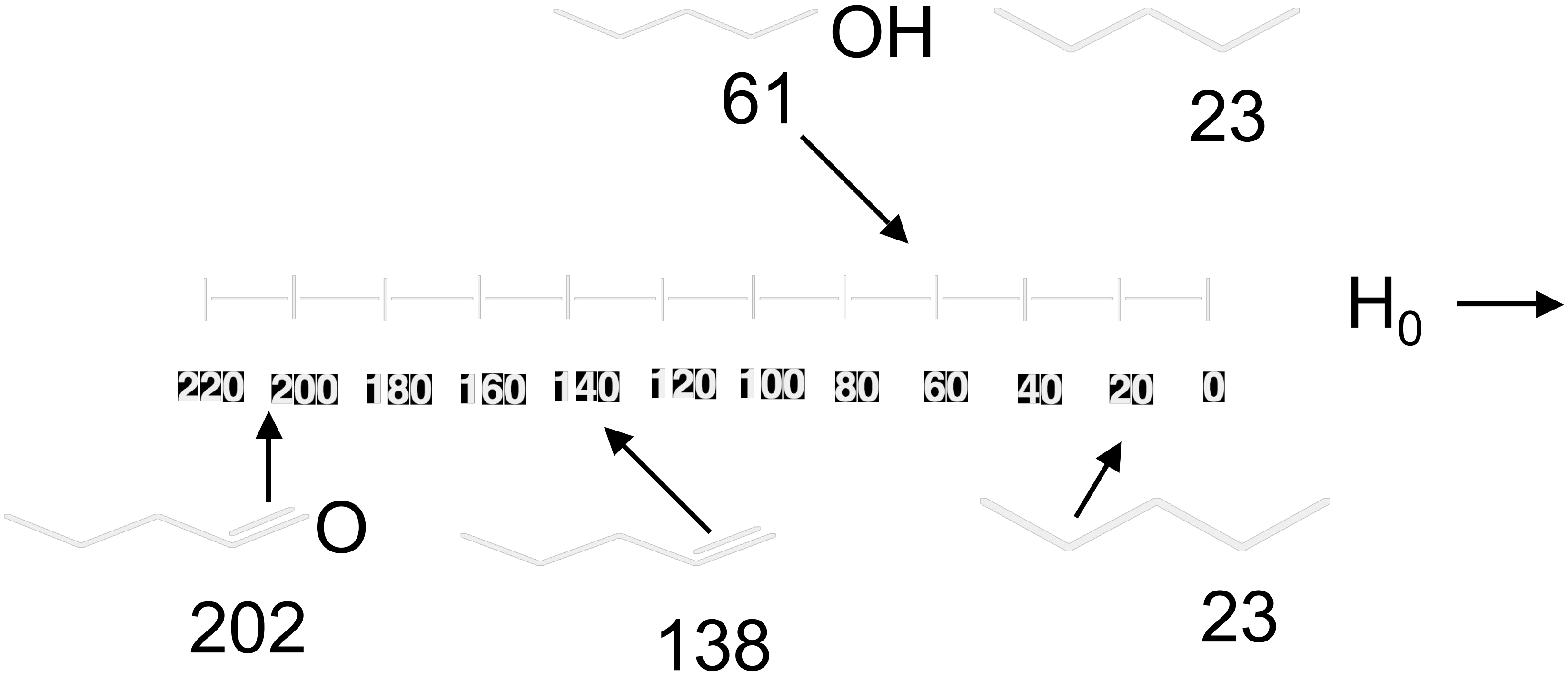
^{13}C Chemical shifts are most affected by:

- hybridization state of carbon
- electronegativity of groups attached to carbon


Increasing electronegativity

$H_0 \longrightarrow$

As the atom attached to a carbon becomes more electronegative, the carbon atom signal is observed at lower field



sp^2 hybridized carbon is at lower field than *sp*^{3}