Chapter 13
Spectroscopy

Infrared spectroscopy

Ultraviolet-Visible spectroscopy

Nuclear magnetic resonance spectroscopy

Mass Spectrometry

13.1

Principles of Molecular Spectroscopy: Electromagnetic Radiation

Electromagnetic Radiation

is propagated at the speed of light

has properties of particles and waves

the energy of a photon is proportional to its frequency

Figure 13.1: The Electromagnetic Spectrum

Shorter Wavelength (l)

Longer Wavelength (l)

Higher Frequency (n)

Lower Frequency (n)

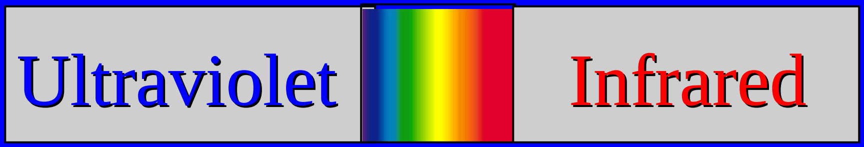
Higher Energy (E)

Lower Energy (E)

Figure 13.1: The Electromagnetic Spectrum

Shorter Wavelength (*l*)

Longer Wavelength (*l*)



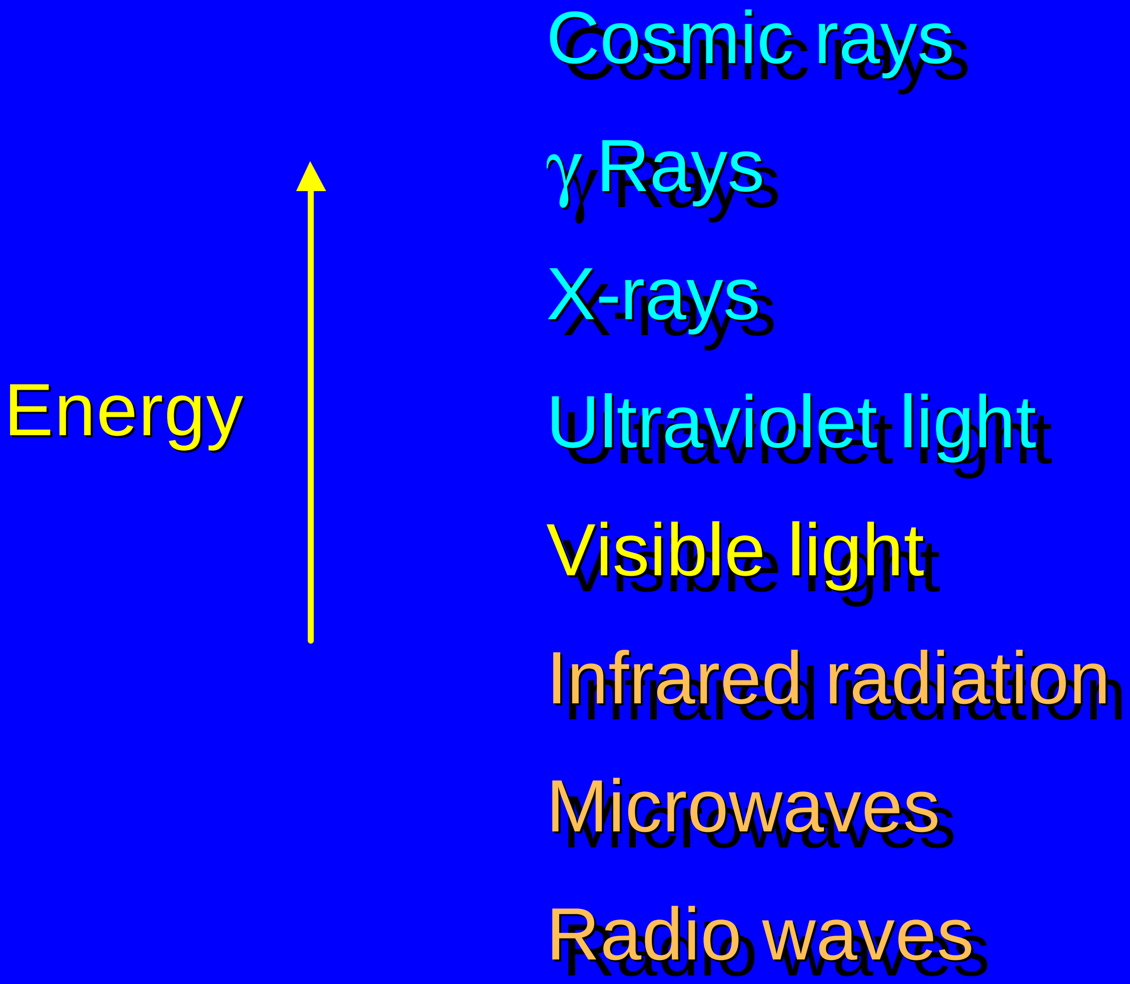
Higher Frequency (*n*)

Lower Frequency (*n*)

Higher Energy (*E*)

Lower Energy (*E*)

Figure 13.1: The Electromagnetic Spectrum



Energy

Cosmic rays

γ Rays

X-rays

Ultraviolet light

Visible light

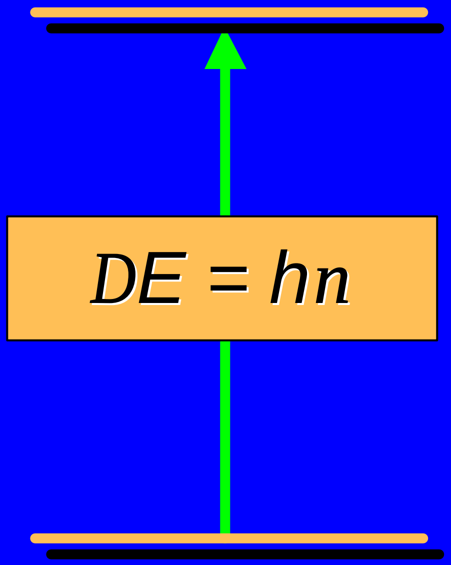
Infrared radiation

Microwaves

Radio waves

13.2

Principles of Molecular Spectroscopy: Quantized Energy States



$$DE = hn$$

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

13.3

Introduction to

^{1}H NMR Spectroscopy

The nuclei that are most useful to organic chemists are:

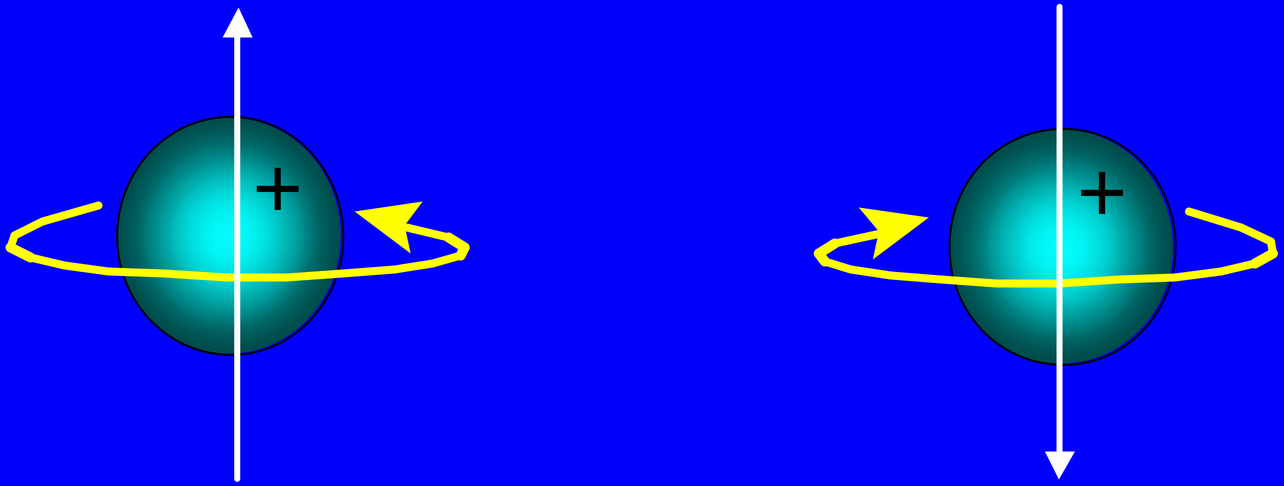
^{1}H and ^{13}C

both have spin = ±1/2

^{1}H is 99% at natural abundance

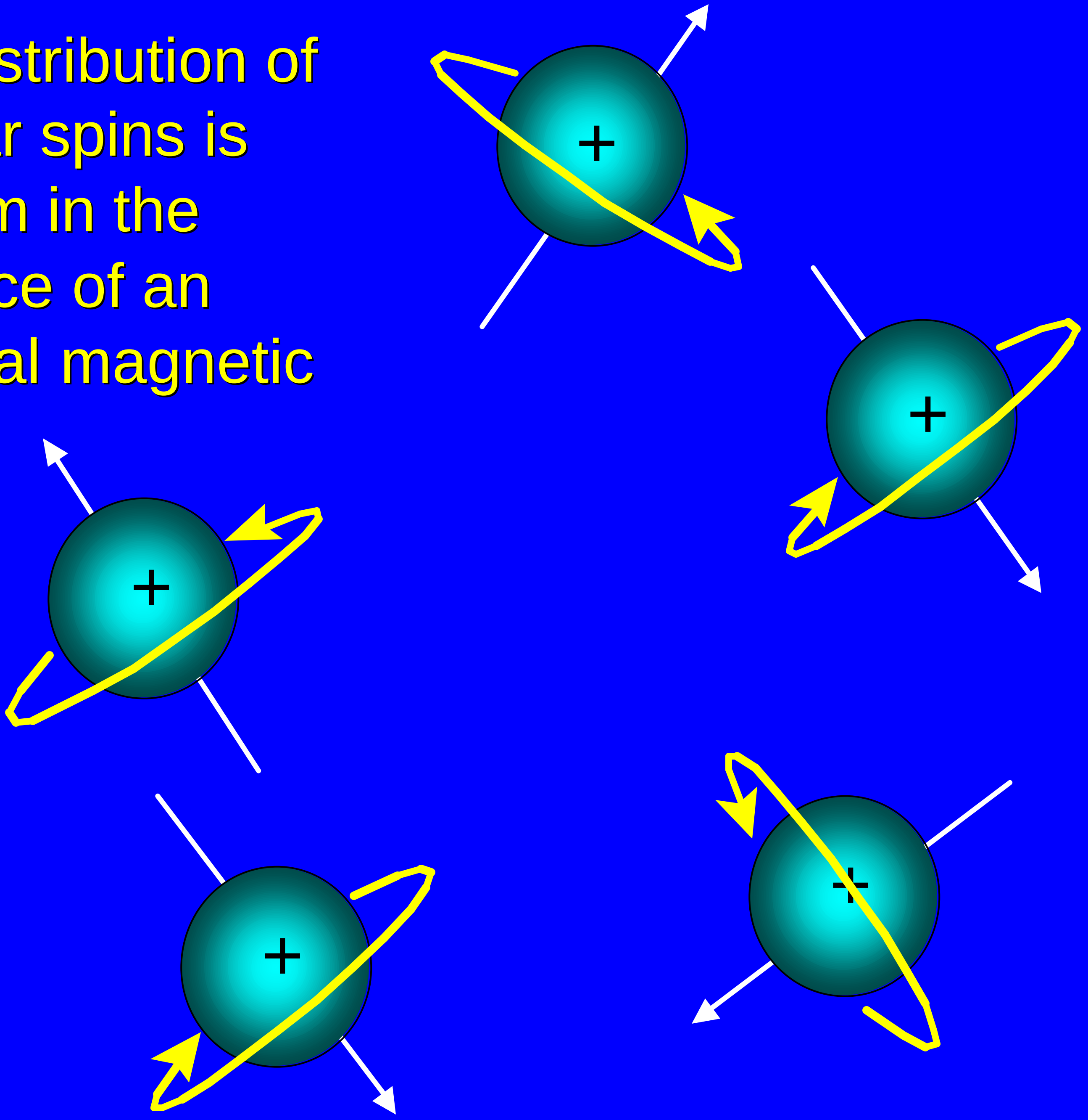
^{13}C is 1.1% at natural abundance

Nuclear Spin

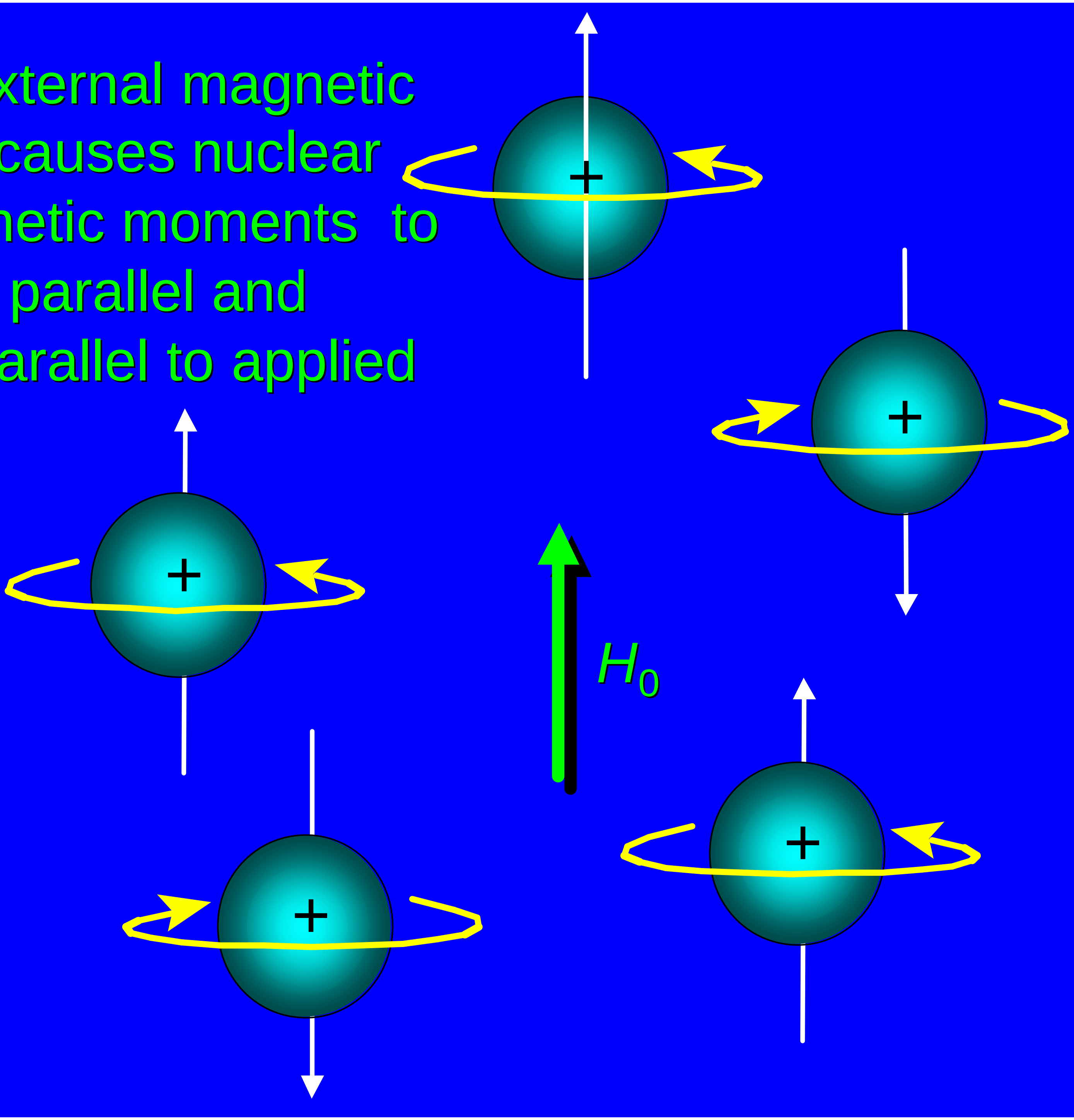


A spinning charge, such as the nucleus of ^{1}H or ^{13}C, generates a magnetic field. The magnetic field generated by a nucleus of spin +1/2 is opposite in direction from that generated by a nucleus of spin –1/2.

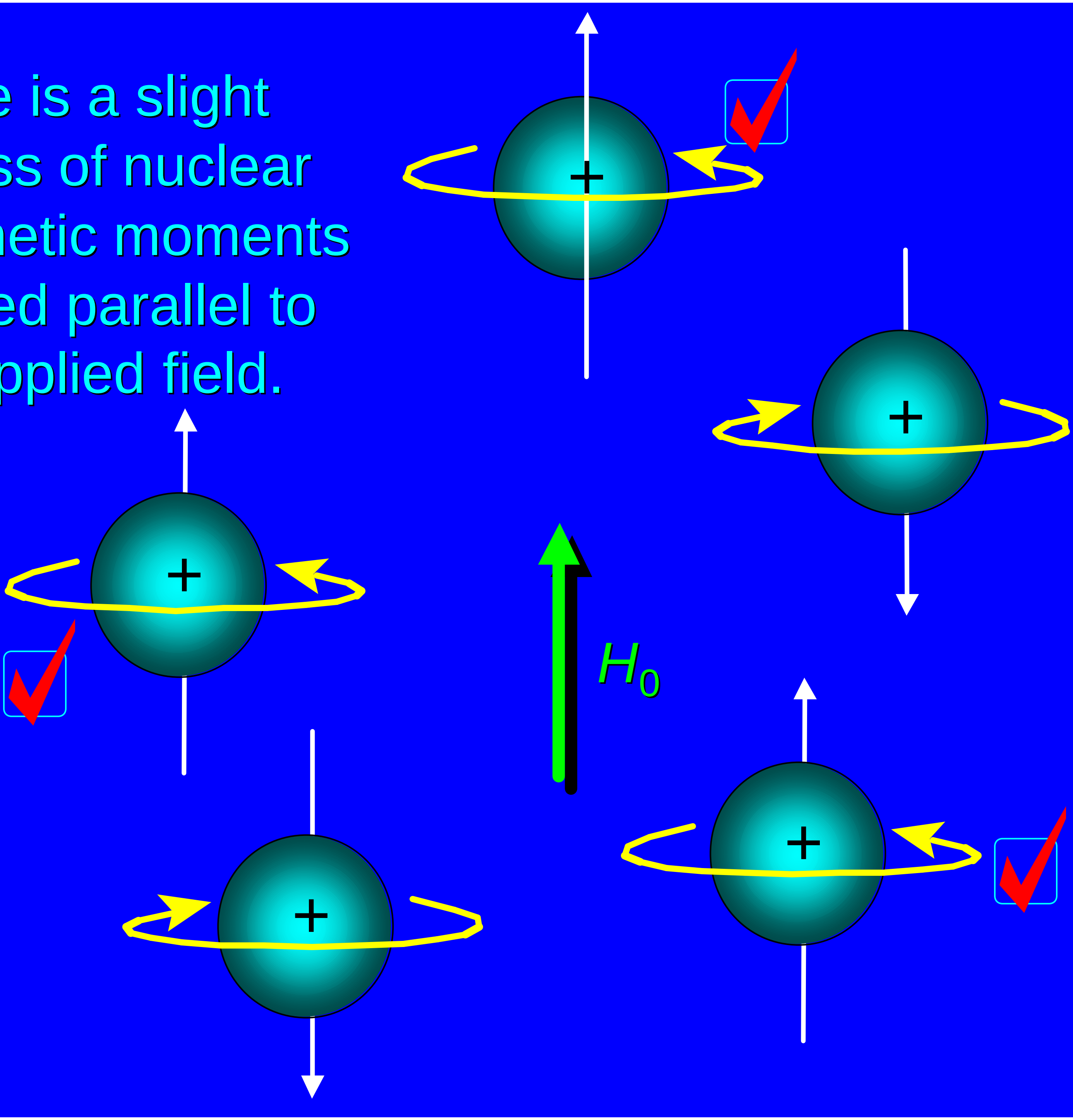
The distribution of nuclear spins is random in the absence of an external magnetic field.



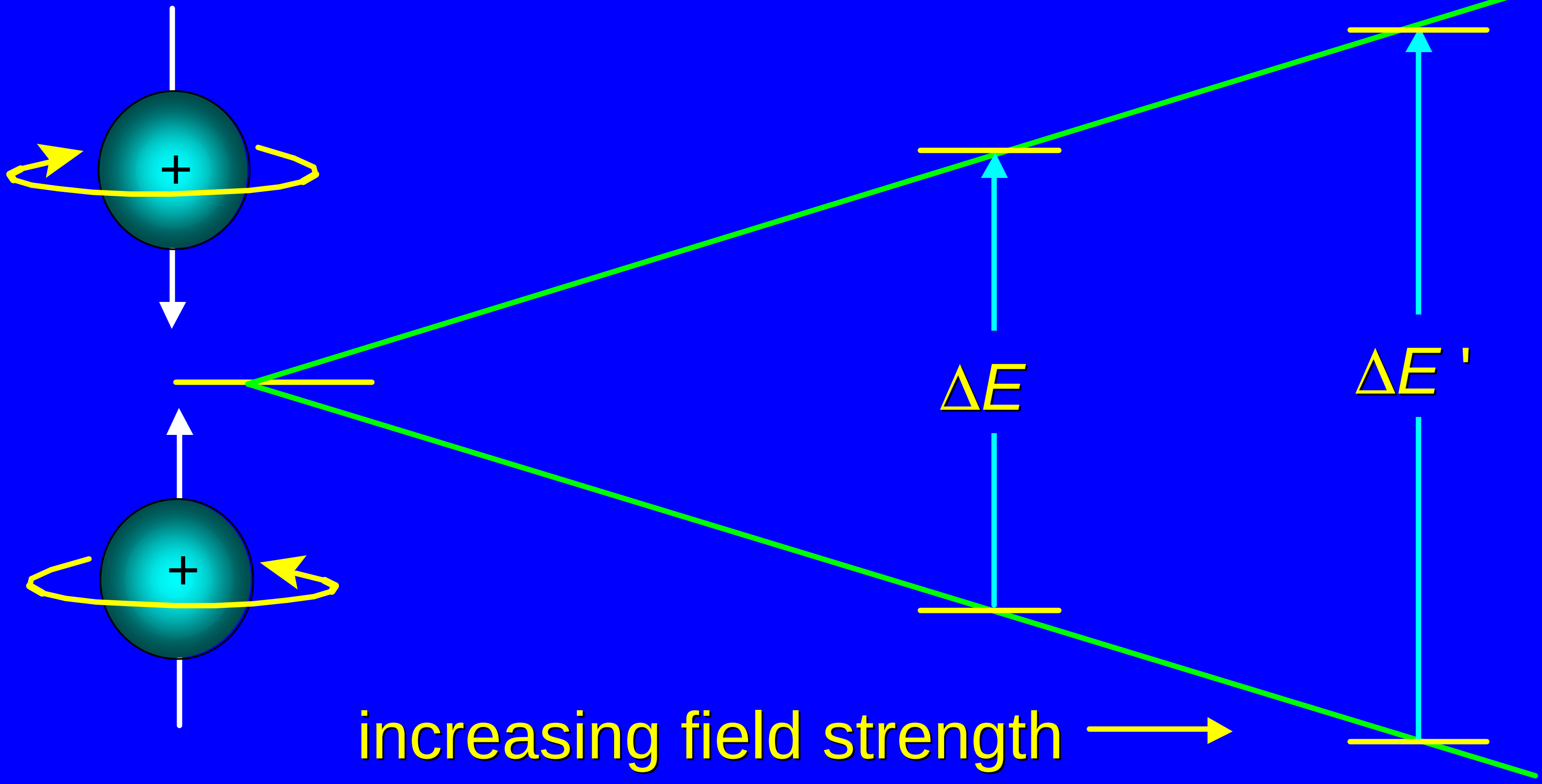
An external magnetic field causes nuclear magnetic moments to align parallel and antiparallel to applied field.



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



Energy Differences Between Nuclear Spin States



increasing field strength →

no 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 of absorbed electromagnetic radiation is proportional to	Hz
the energy difference between two nuclear spin states which is proportional to	kJ/mol (kcal/mol)
the applied magnetic field	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 4.7 T:

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

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

Some important relationships in NMR

The frequency of absorbed electromagnetic radiation for a particular nucleus (such as ^{1}H) depends on its molecular environment.

This is why NMR is such a useful tool for structure determination.

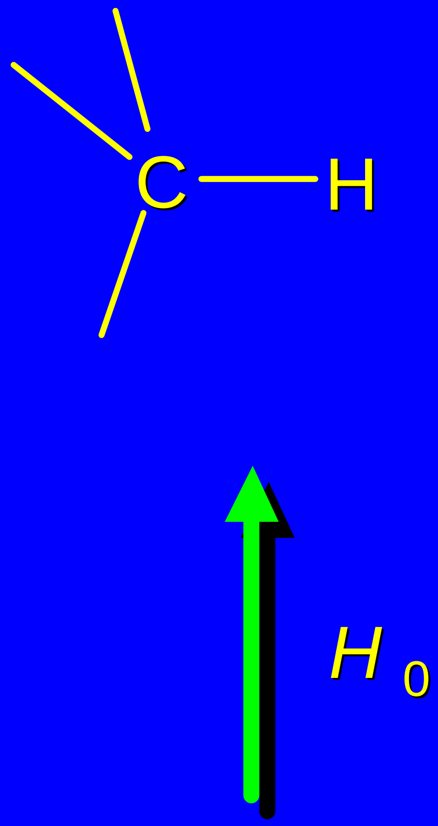
13.4
Nuclear Shielding
and
^{1}H Chemical Shifts

What do we mean by "shielding?"

What do we mean by "chemical shift?"

Shielding

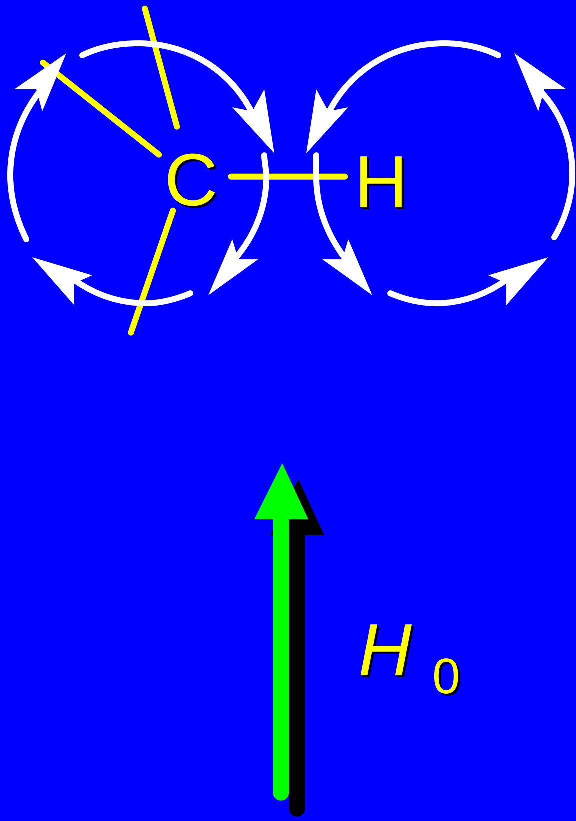
An external magnetic field affects the motion of the electrons in a molecule, inducing a magnetic field within the molecule.



Shielding

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

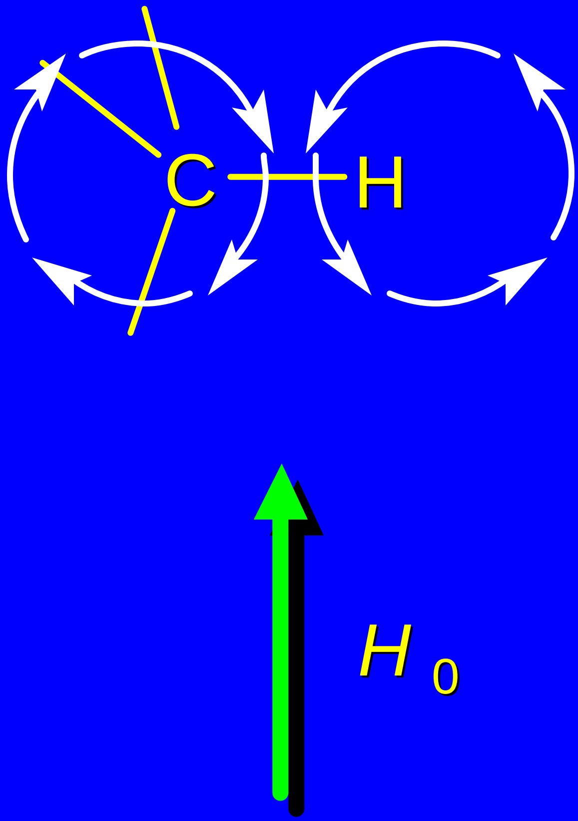
The direction of the induced magnetic field is opposite to that of the applied field.



Shielding

The induced field shields the nuclei (in this case, C and H) from the applied field.

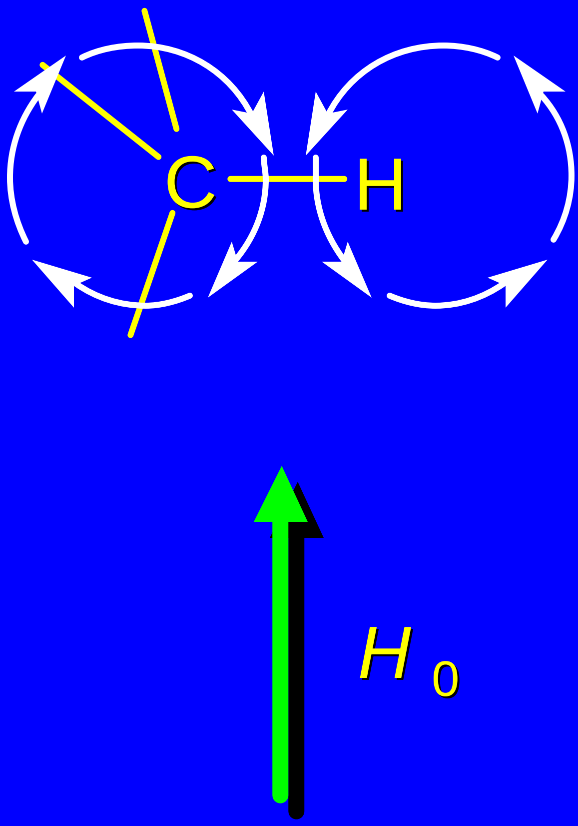
A stronger external field is needed in order for energy difference between spin states to match energy of rf radiation.

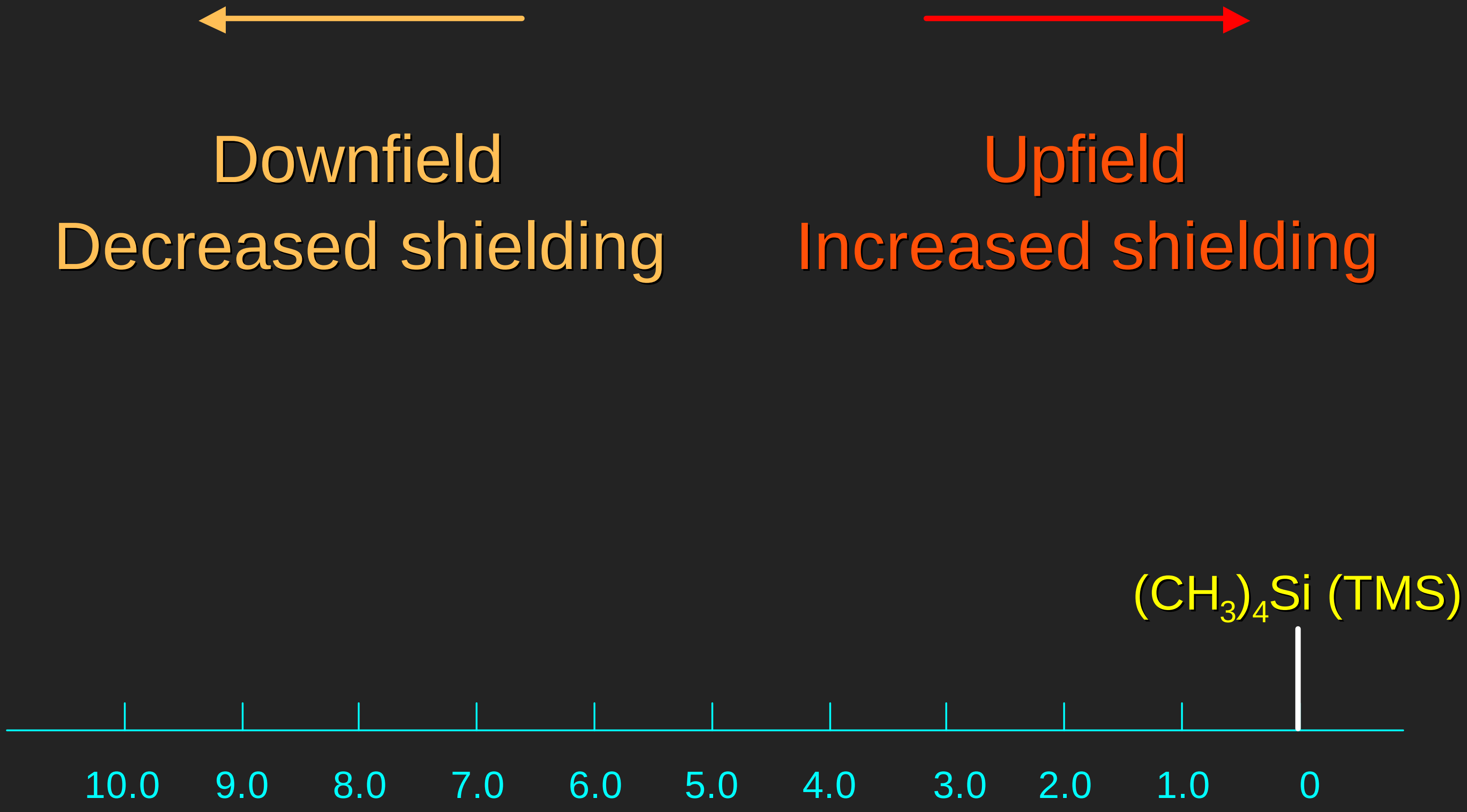


Chemical Shift

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.

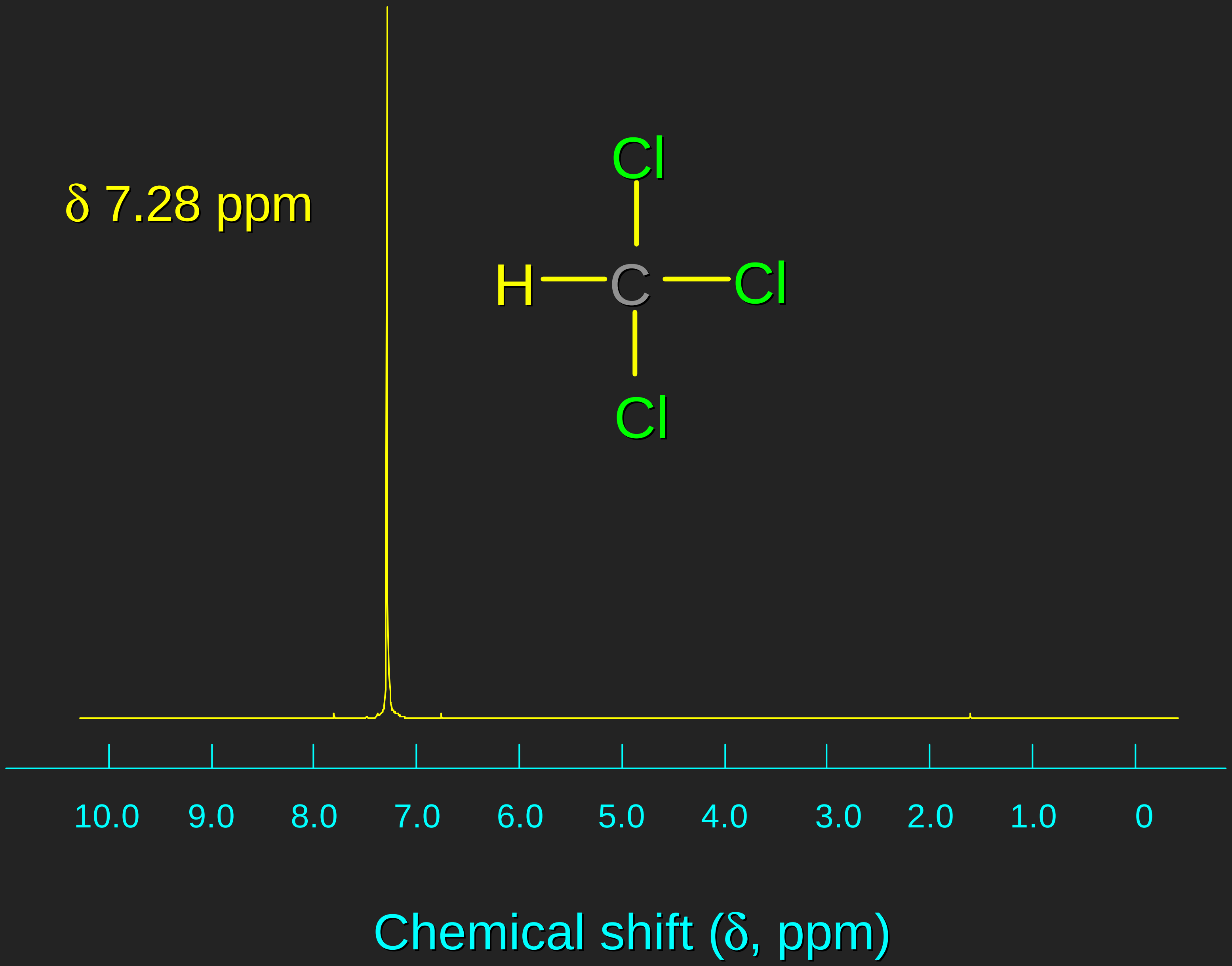




Downfield
Decreased shielding

Upfield
Increased shielding

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
Chemical shift (δ, ppm)

13.5
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

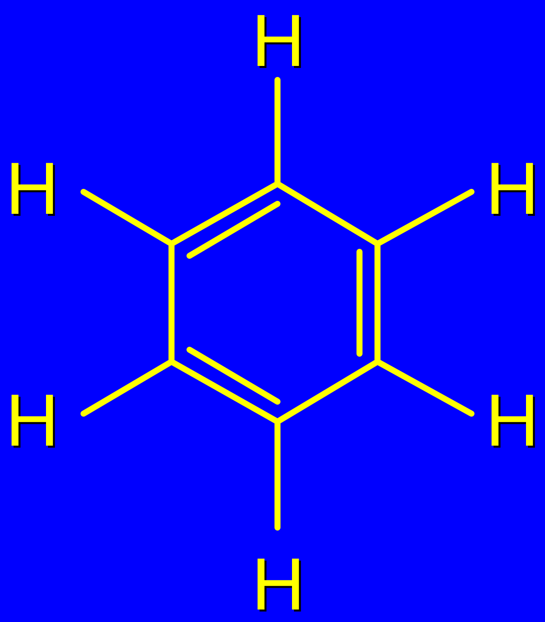
Electronegative substituents decrease the shielding of methyl groups

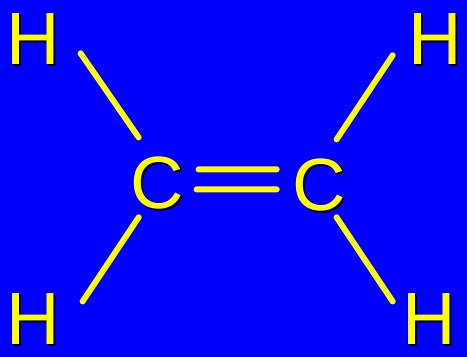
CH_3F	δ 4.3 ppm	*least shielded H*
CH_3OCH_3	δ 3.2 ppm	
$CH_3N(CH_3)_2$	δ 2.2 ppm	
CH_3CH_3	δ 0.9 ppm	
$CH_3Si(CH_3)_3$	δ 0.0 ppm	*most shielded H*

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





CH_3CH_3

δ 7.3 ppm

δ 5.3 ppm

δ 0.9 ppm

Table 13.1 (p 496)

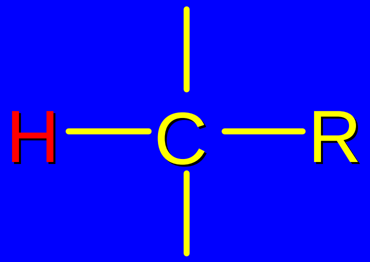
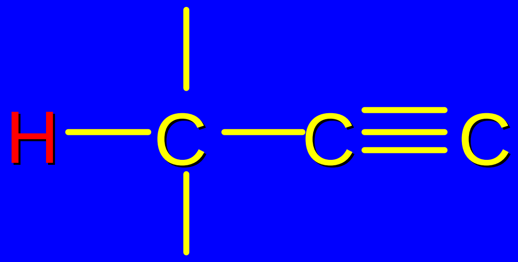
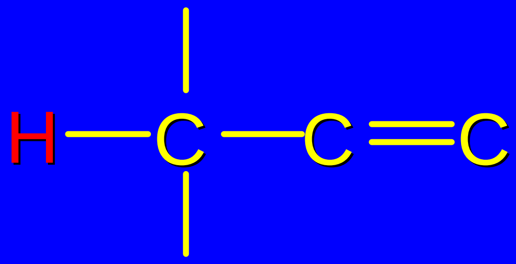
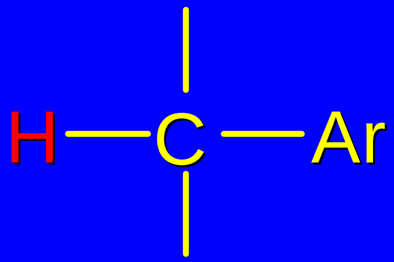
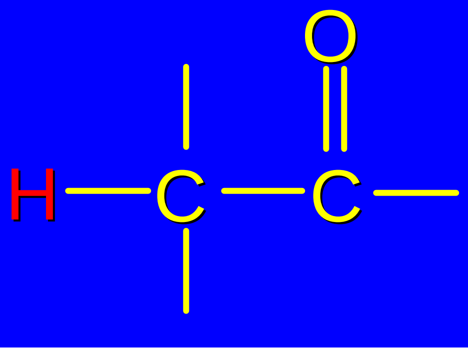
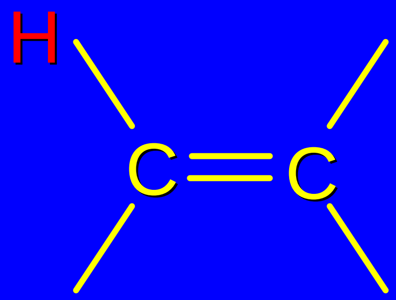
Type of proton	Chemical shift (δ), ppm	Type of proton	Chemical shift (δ), ppm
	0.9-1.8		2.5
	1.6-2.6		2.3-2.8
	2.1-2.5		4.5-6.5

Table 13.1 (p 496)

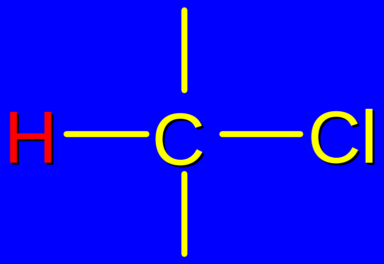
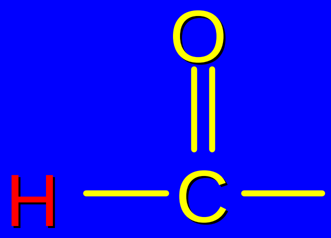
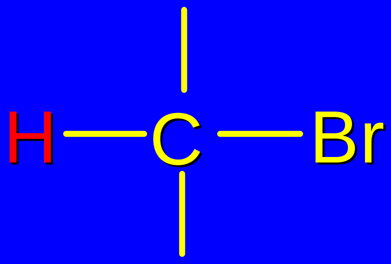
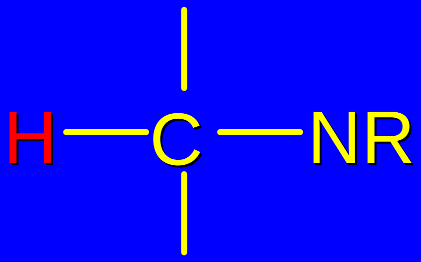
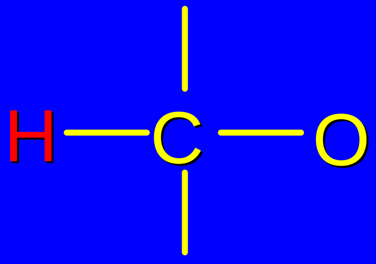
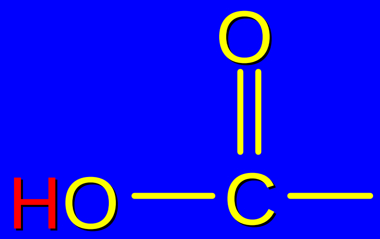
Type of proton	Chemical shift (δ), ppm	Type of proton	Chemical shift (δ), ppm
H—Ar	6.5-8.5	 $\mathrm{H-\overset{\mid}{\underset{\mid}{C}}-Cl}$	3.1-4.1
 $\mathrm{H-\overset{\overset{O}{\|}}{C}-}$	9-10	 $\mathrm{H-\overset{\mid}{\underset{\mid}{C}}-Br}$	2.7-4.1
 $\mathrm{H-\overset{\mid}{\underset{\mid}{C}}-NR}$	2.2-2.9	 $\mathrm{H-\overset{\mid}{\underset{\mid}{C}}-O}$	3.3-3.7

Table 13.1 (p 496)

Type of proton	Chemical shift (δ), ppm
H—NR	1-3
H—OR	0.5-5
H—OAr	6-8
 $HO-\overset{O}{\overset{\|}{C}}-$	10-13