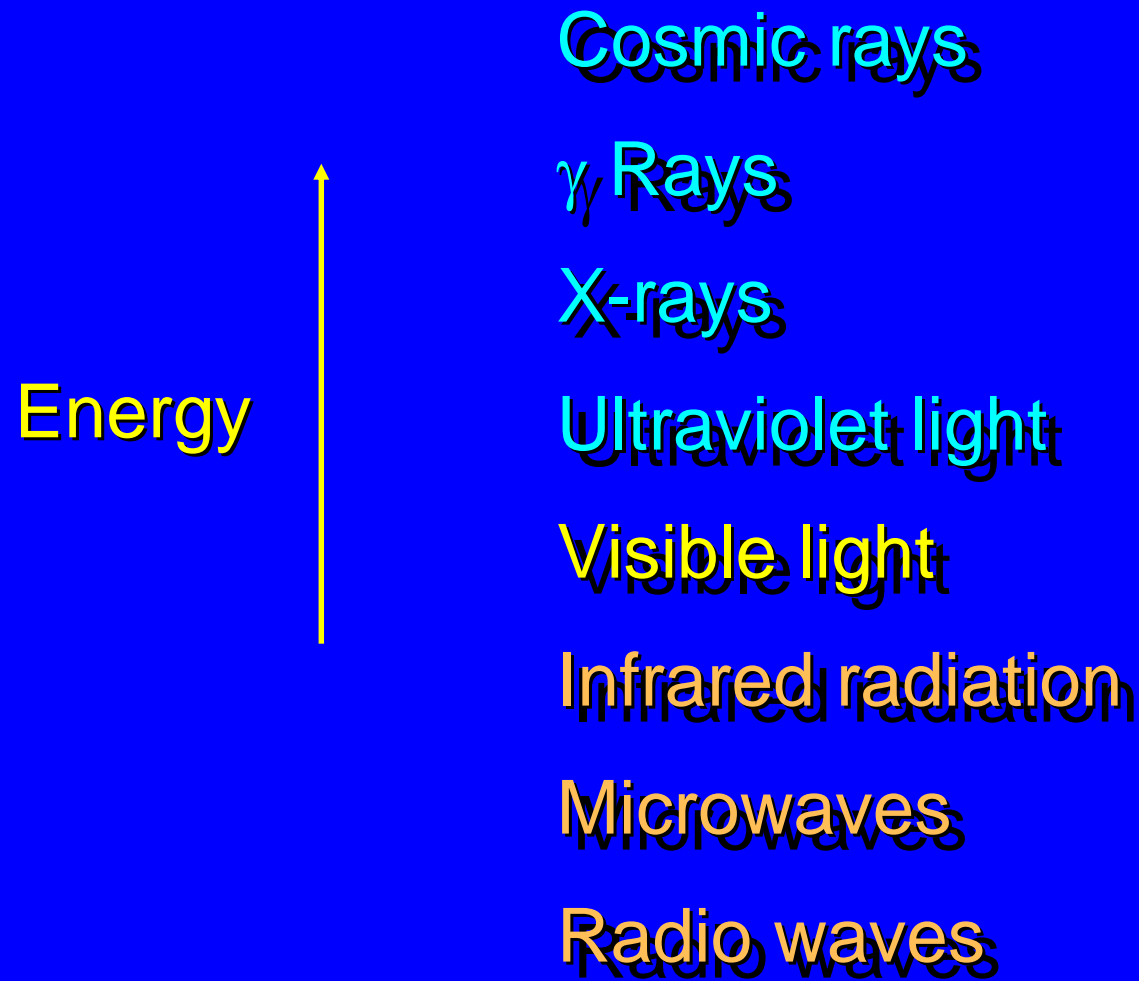


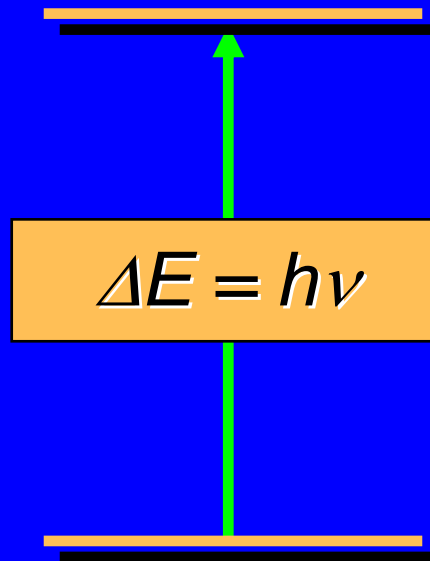
# **Spectroscopy**

**Infrared spectroscopy**

**Nuclear magnetic resonance spectroscopy**

# Figure 13.1: The Electromagnetic Spectrum





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

# **$^1\text{H}$ NMR Spectroscopy**

*The Nuclei that are Most Useful to  
Organic Chemists are:*

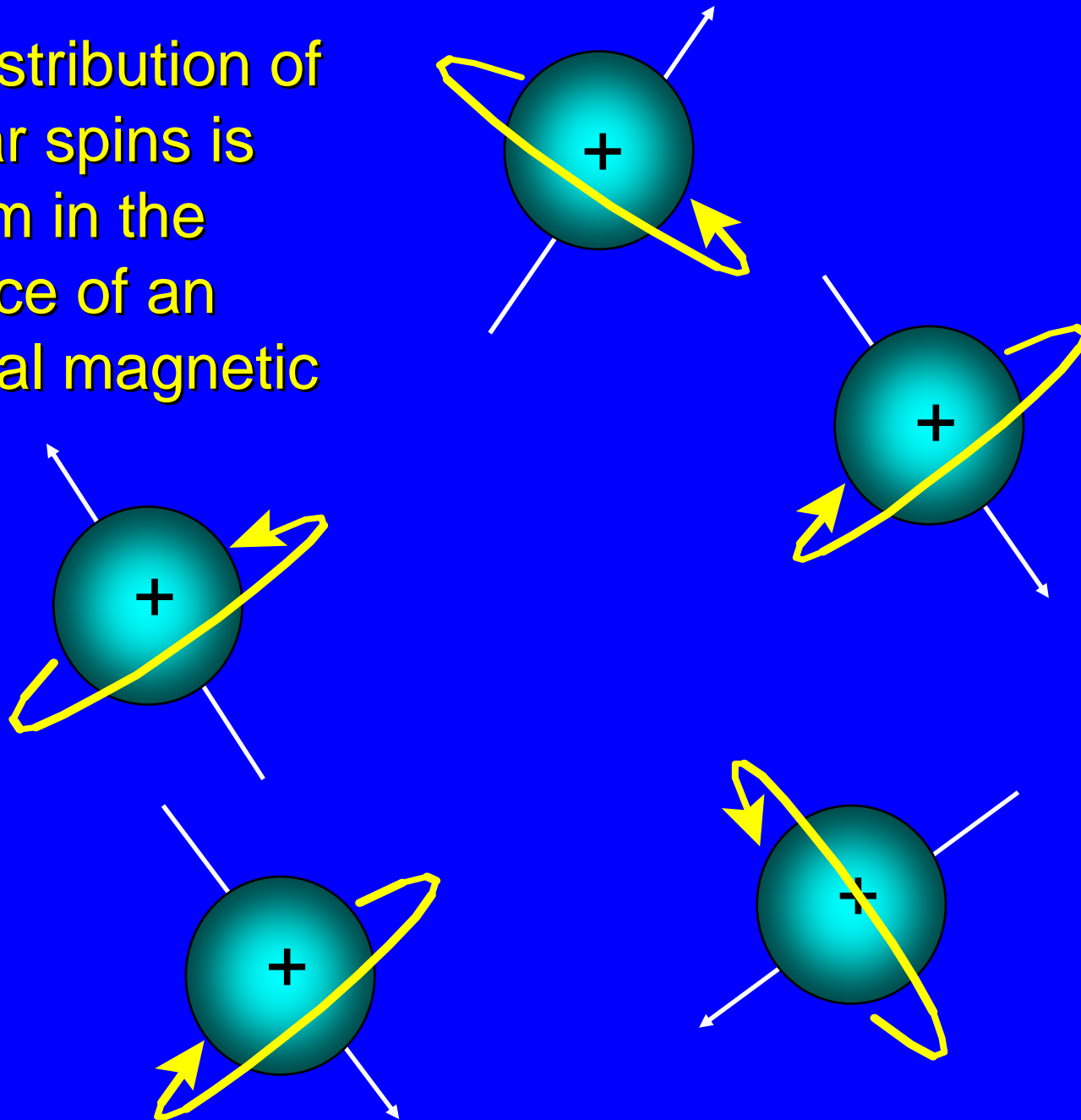
$^1\text{H}$  and  $^{13}\text{C}$

both have spin =  $\pm 1/2$

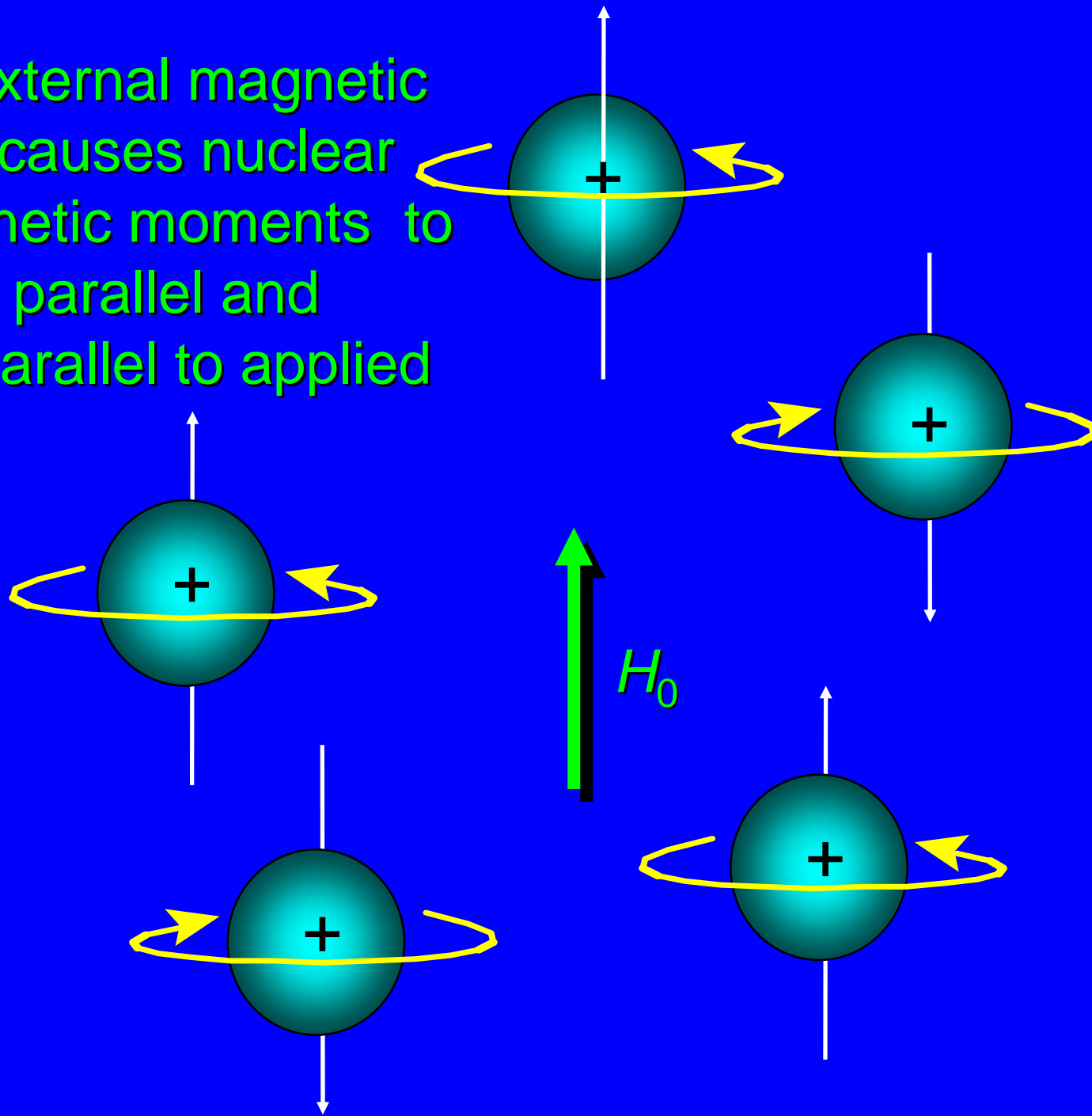
$^1\text{H}$  is 99% at natural abundance

$^{13}\text{C}$  is 1.1% at natural abundance

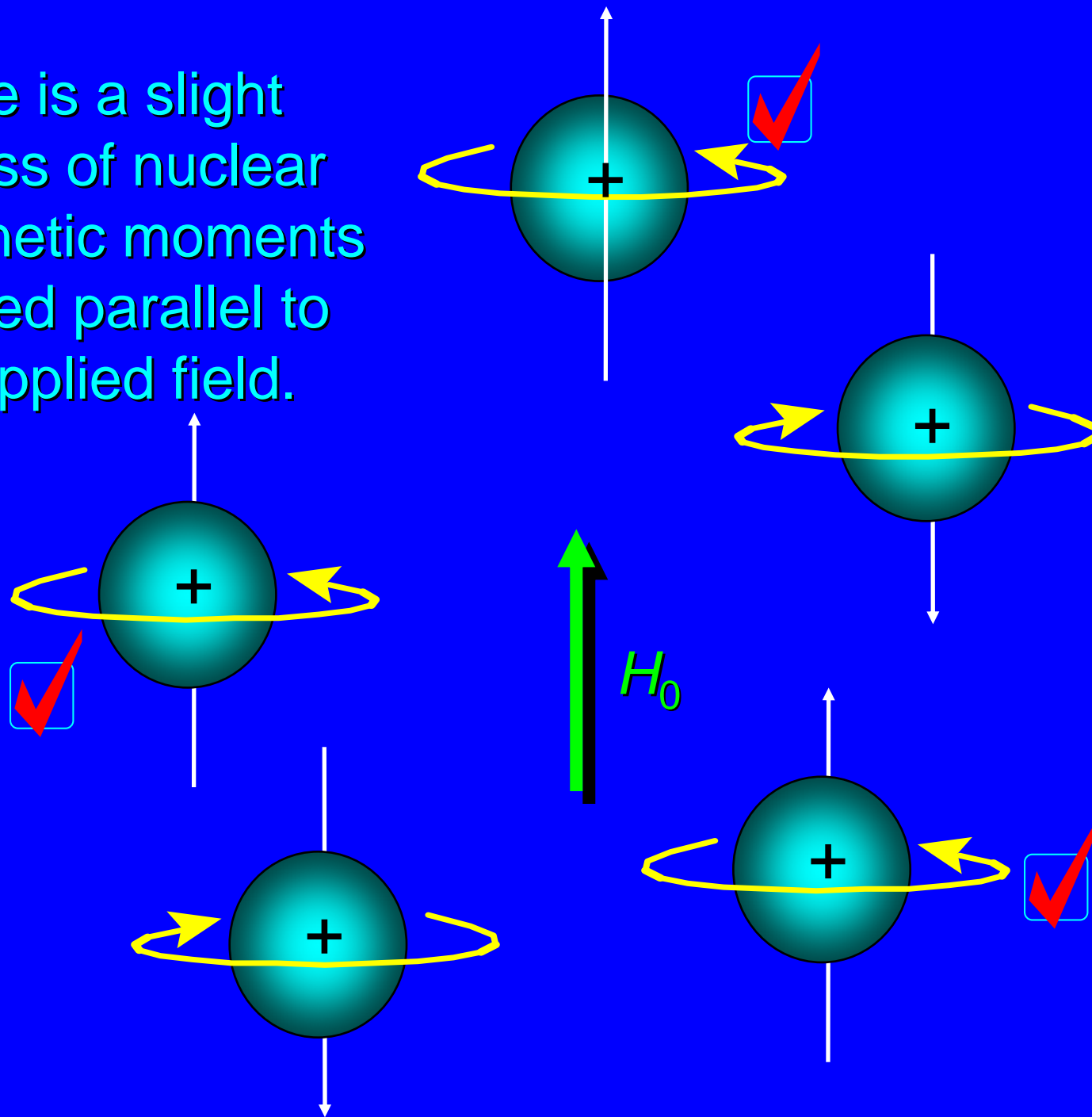
The distribution of nuclear spins is random in the absence of an external magnetic field.



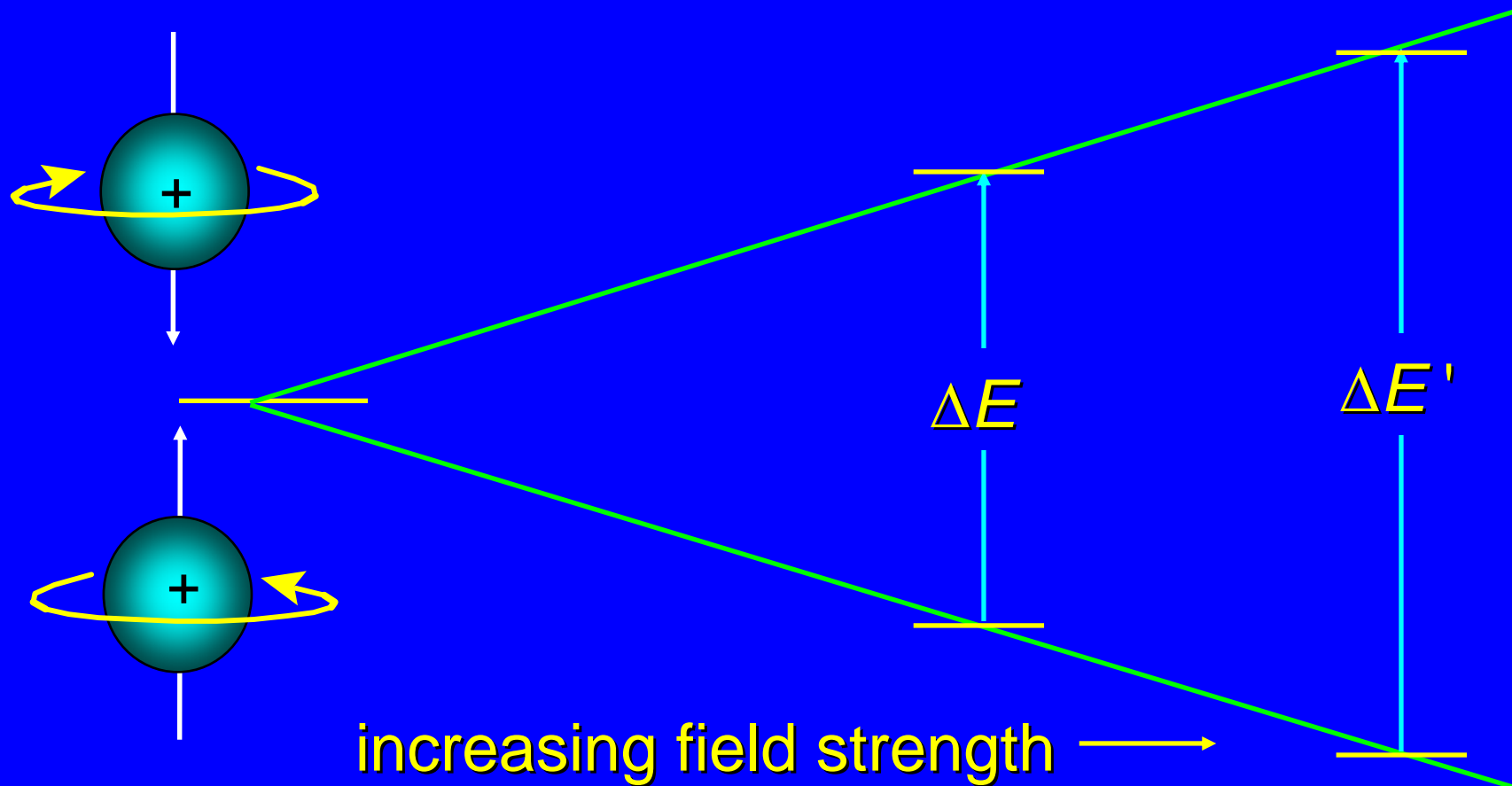
An external magnetic field causes nuclear magnetic moments to align parallel and antiparallel to applied field.



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



# Energy Differences Between Nuclear Spin States



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 for a particular nucleus (such as  $^1\text{H}$ ) depends on its molecular environment.

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

# Nuclear Shielding and $^1\text{H}$ Chemical Shifts

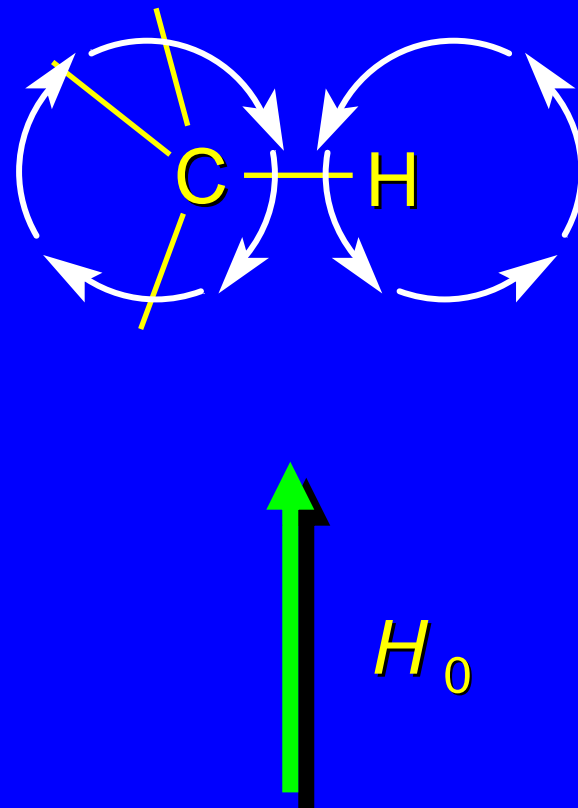
What do we mean by "shielding"?

What do we mean by "chemical shift"?

## Shielding

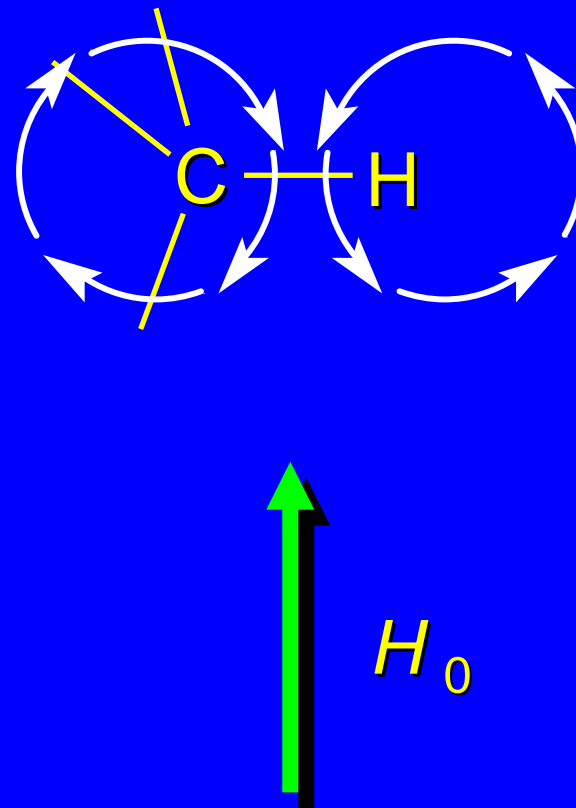
An external magnetic field affects the motion of the electrons in a molecule, inducing a magnetic field within the molecule.

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



## Shielding

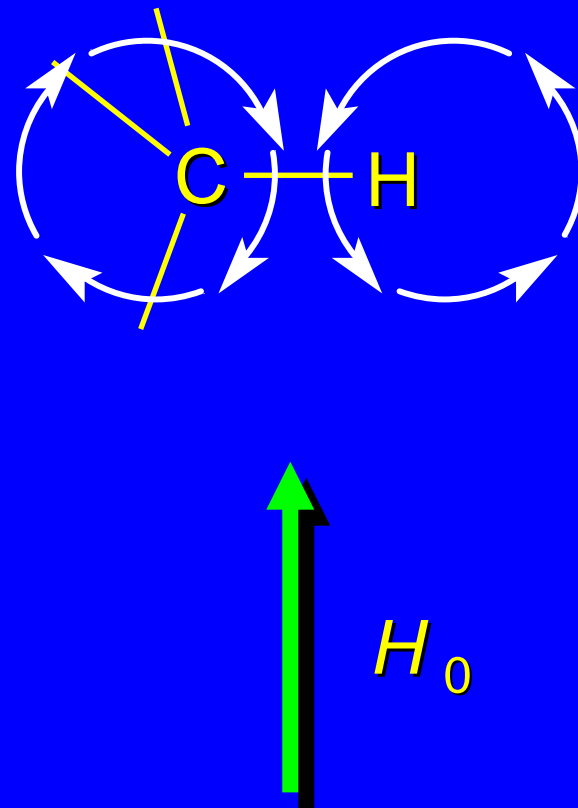
The induced field shields the nuclei (in this case, C and H) from the applied field.



## Chemical Shift

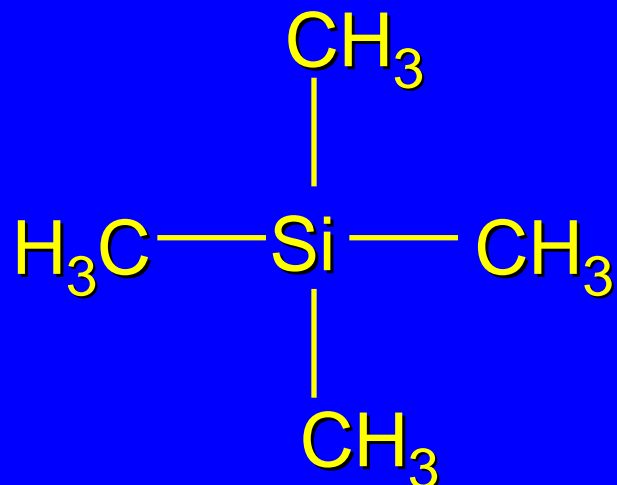
Chemical shift is a measure of the degree to which a nucleus in a molecule is shielded.

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

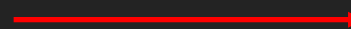


## Chemical Shift

Chemical shifts ( $\delta$ ) are measured relative to the protons in tetramethylsilane (TMS) as a standard.



$$\delta = \frac{\text{position of signal} - \text{position of TMS peak}}{\text{spectrometer frequency}} \times 10^6$$

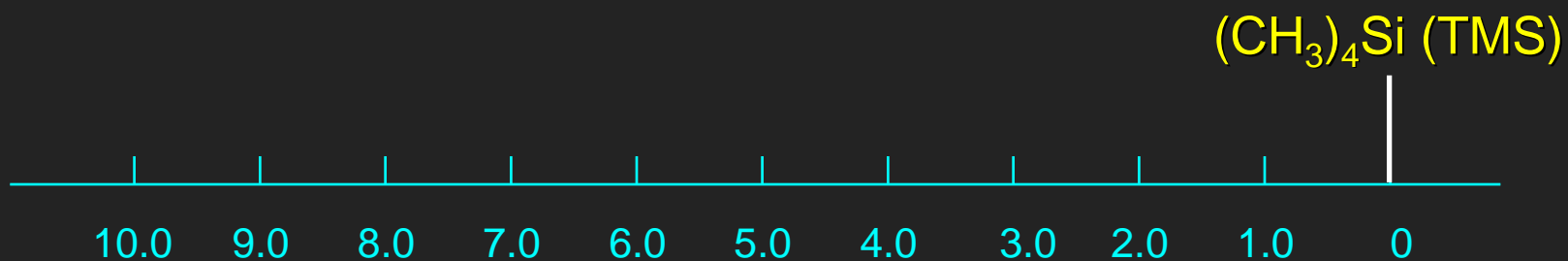


Downfield

Upfield

Decreased shielding

Increased shielding



Chemical shift ( $\delta$ , ppm)  
measured relative to TMS

## Chemical Shift

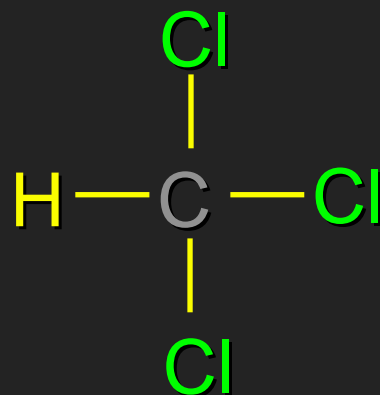
Example: The signal for the proton in chloroform ( $\text{HCCl}_3$ ) appears 1456 Hz downfield from TMS at a spectrometer frequency of 200 MHz.

$$\delta = \frac{\text{position of signal} - \text{position of TMS peak}}{\text{spectrometer frequency}} \times 10^6$$

$$\delta = \frac{1456 \text{ Hz} - 0 \text{ Hz}}{200 \times 10^6 \text{ Hz}} \times 10^6$$

$$\delta = 7.28$$

$\delta$  7.28 ppm



Chemical shift ( $\delta$ , ppm)

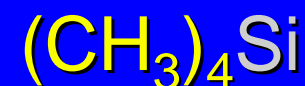
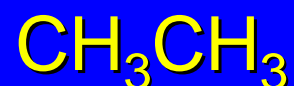
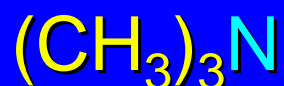
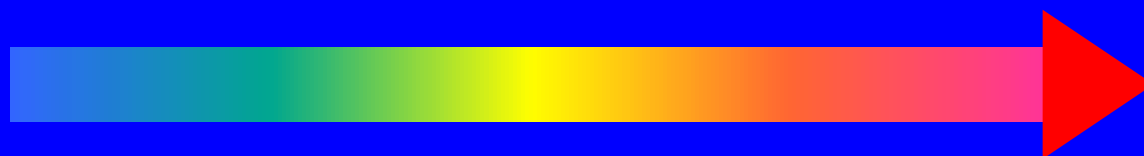
# Effects of Molecular Structure on $^1\text{H}$ Chemical Shifts

Protons in different environments experience different degrees of shielding and have different chemical shifts.

*Electronegative Substituents Decrease  
the Shielding of Methyl Groups*

*least shielded H*

*most shielded H*



$\delta$  4.3

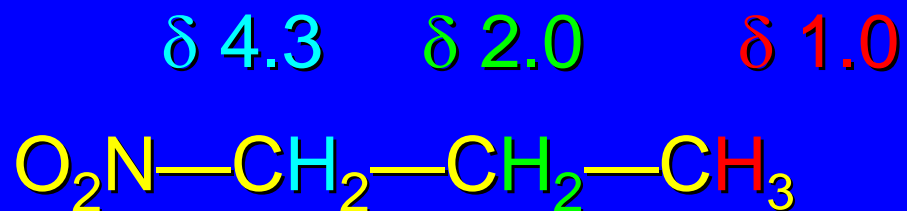
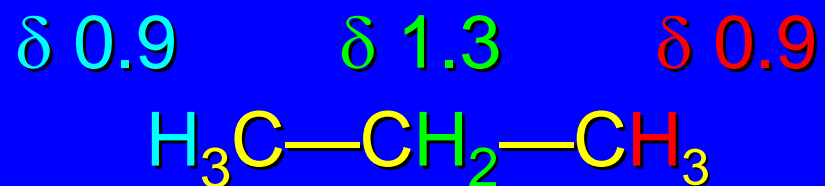
$\delta$  3.2

$\delta$  2.2

$\delta$  0.9

$\delta$  0.0

## *Electronegative Substituents Decrease Shielding*



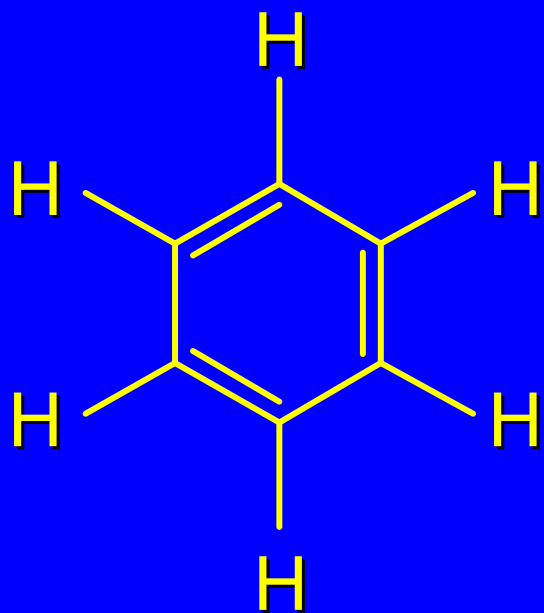
*Effect is Cumulative*

CHCl<sub>3</sub>      δ 7.3

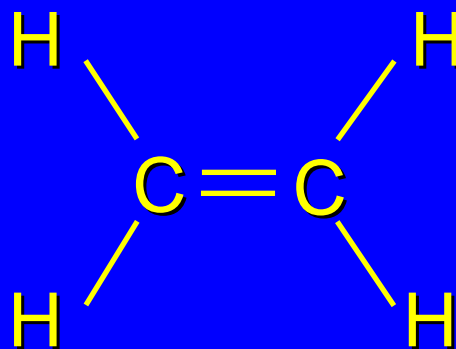
CH<sub>2</sub>Cl<sub>2</sub>      δ 5.3

CH<sub>3</sub>Cl      δ 3.1

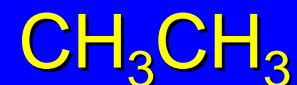
*Protons Attached to  $sp^2$  Hybridized Carbon  
are Less Shielded than those Attached  
to  $sp^3$  Hybridized Carbon*



$\delta$  7.3



$\delta$  5.3



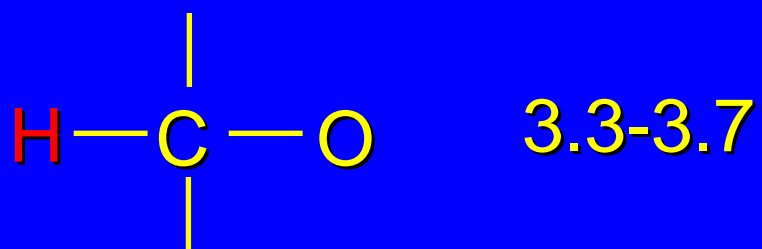
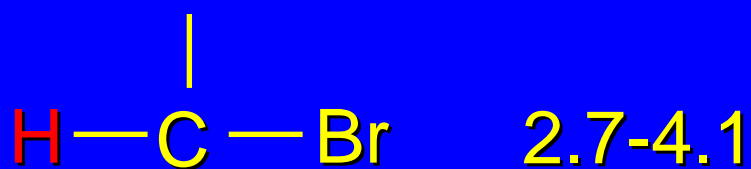
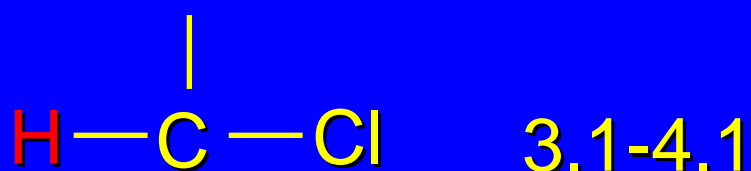
$\delta$  0.9

*Table 13.1*

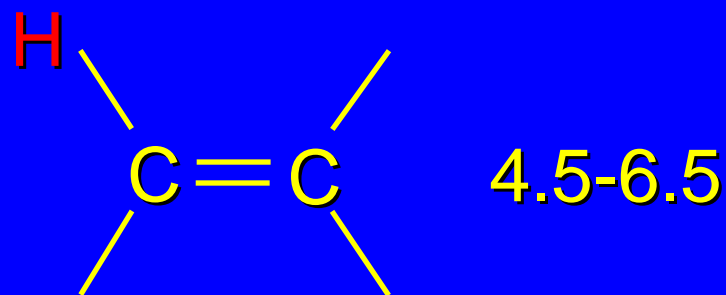
Type of proton	Chemical shift ( $\delta$ ), ppm	Type of proton	Chemical shift ( $\delta$ ), ppm
$\begin{array}{c}   \\ \text{H}-\text{C}-\text{R} \\   \end{array}$	0.9-1.8	$\begin{array}{c}   \\ \text{H}-\text{C}-\text{C}\equiv\text{N} \\   \end{array}$	2.1-2.3
$\begin{array}{c}   \\ \text{H}-\text{C}-\text{C}=\text{C} \\   \end{array}$	1.5-2.6	$\begin{array}{c}   \\ \text{H}-\text{C}-\text{C}\equiv\text{C} \\   \end{array}$	2.5
$\begin{array}{c}   & \text{O} \\   &    \\ \text{H}-\text{C}-\text{C}- \\   & \end{array}$	2.0-2.5	$\begin{array}{c}   \\ \text{H}-\text{C}-\text{Ar} \\   \end{array}$	2.3-2.8

*Table 13.1*

Type of proton      Chemical shift ( $\delta$ ),  
ppm



Type of proton      Chemical shift ( $\delta$ ),  
ppm



*Table 13.1*

Type of proton    Chemical shift ( $\delta$ ),  
ppm

$\text{H}-\text{NR}$             1-3

$\text{H}-\text{OR}$             0.5-5

$\text{H}-\text{OAr}$            6-8

$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-$         10-13

# Interpreting $^1\text{H}$ NMR Spectra

*Information Contained in an NMR  
Spectrum Includes:*

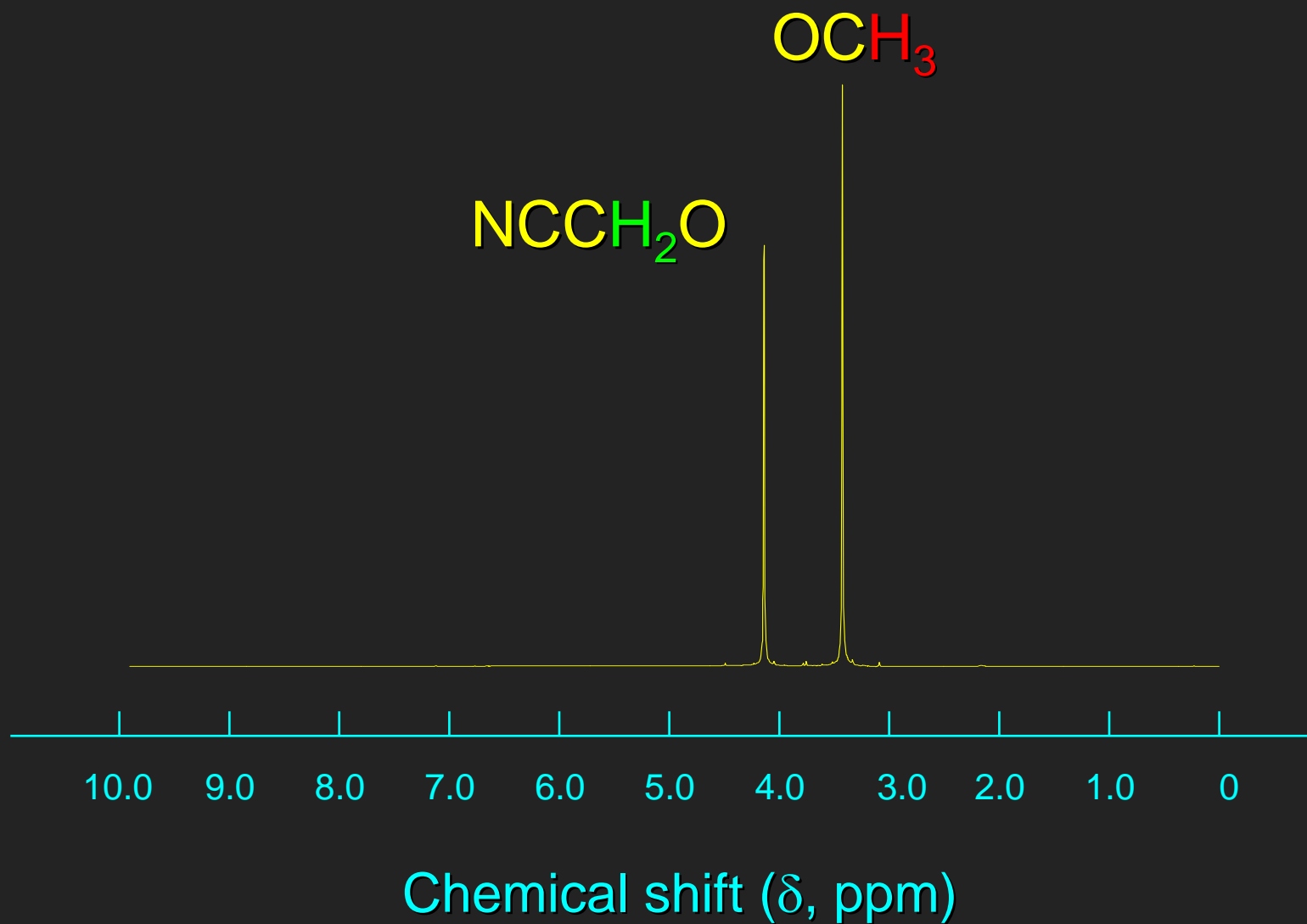
1. Number of signals
2. Their intensity (as measured by area under peak)
3. Splitting pattern (multiplicity)

## *Number of Signals*

Protons that have different chemical shifts are chemically nonequivalent.

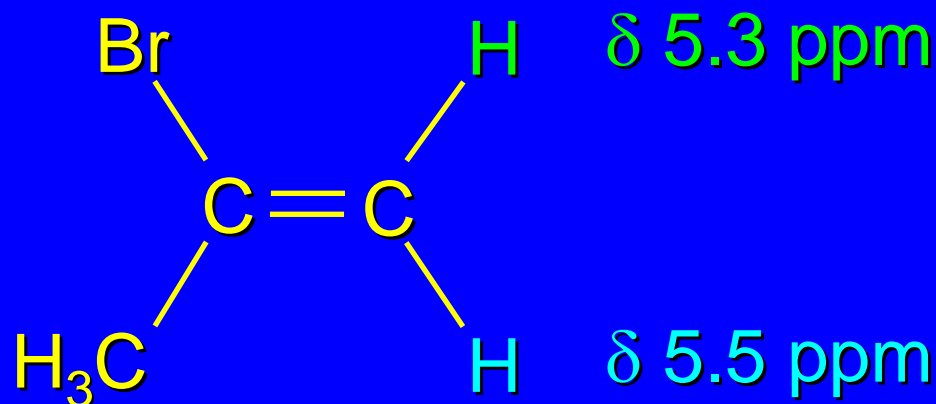
Exist in different molecular environment.

Figure 13.11



## *Diastereotopic Protons*

Diastereotopic protons can have different chemical shifts.

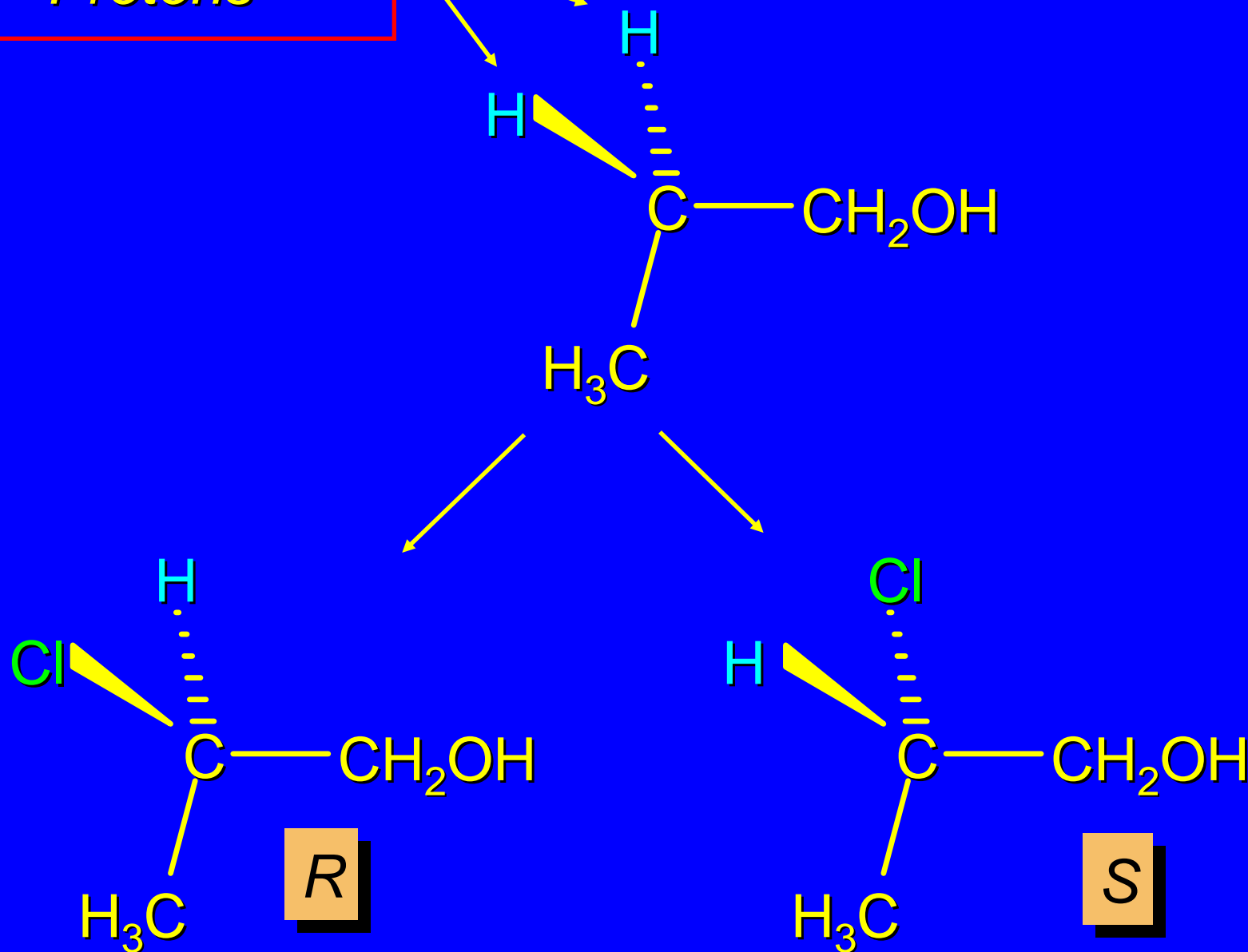


## *Enantiotopic Protons*

Are in mirror-image environments.

Enantiotopic protons have the same chemical shift.

*Enantiotopic  
Protons*



# Spin-Spin Splitting in $^1\text{H}$ NMR Spectroscopy

Not all peaks are singlets.

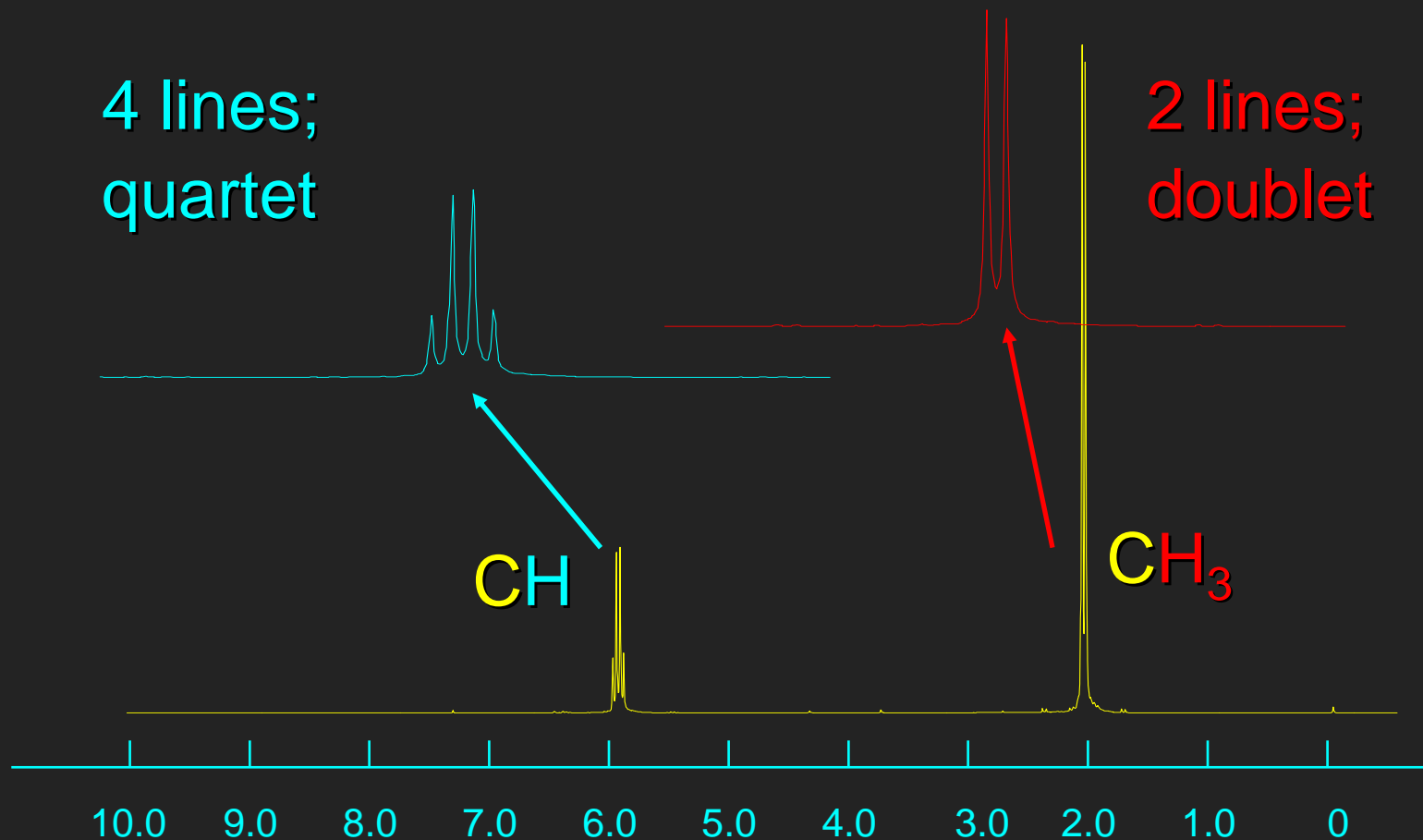
Signals can be split by coupling of  
nuclear spins.

Figure 13.12



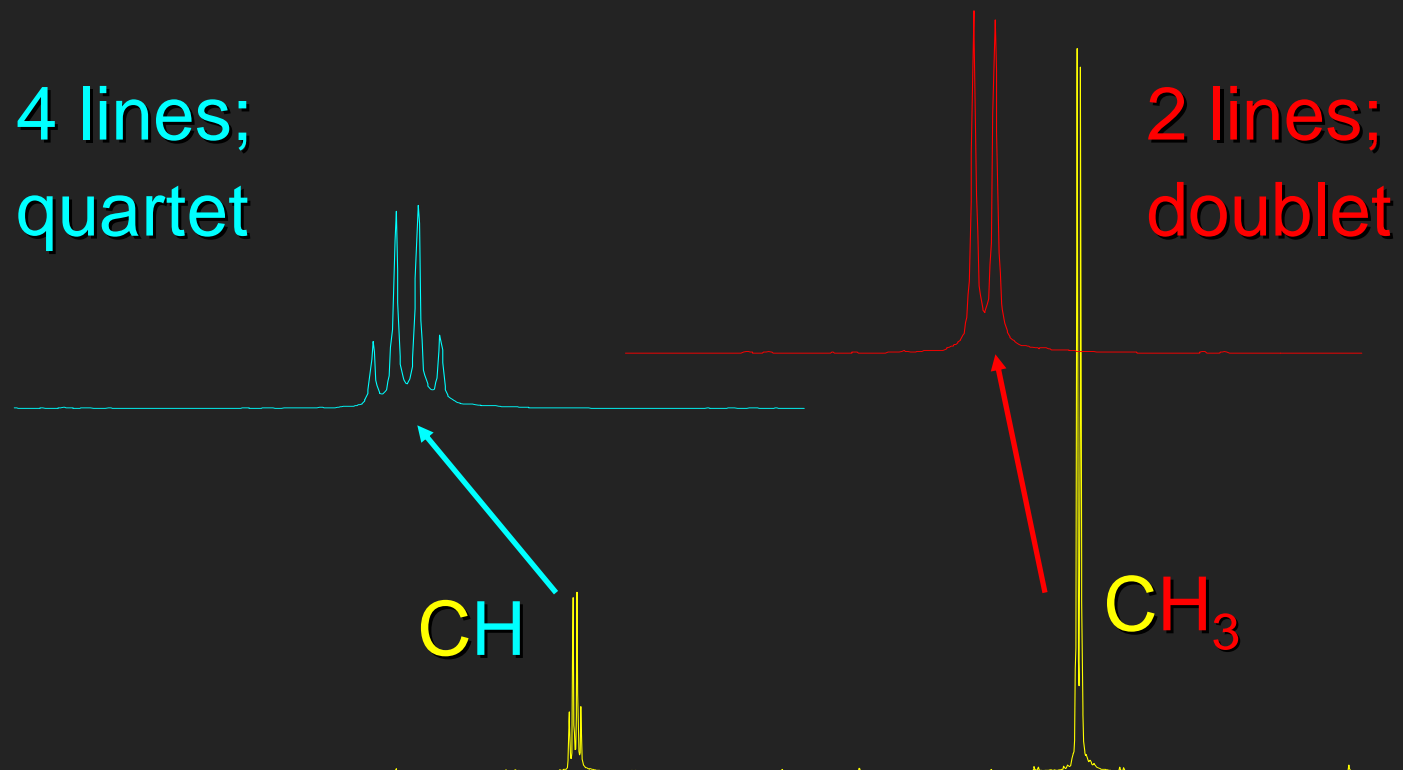
4 lines;  
quartet

2 lines;  
doublet



Chemical shift ( $\delta$ , ppm)

Figure 13.12

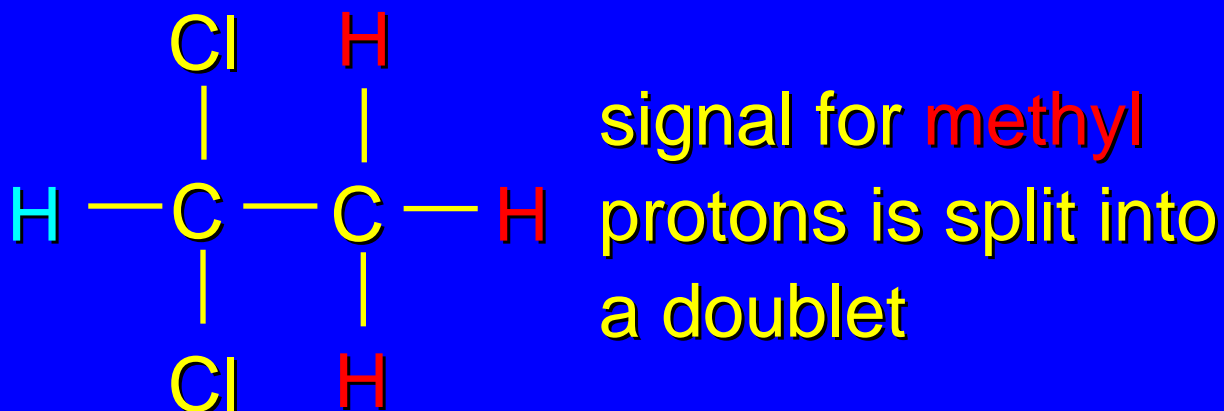


coupled protons are vicinal (three-bond coupling)

CH splits CH<sub>3</sub> into a doublet

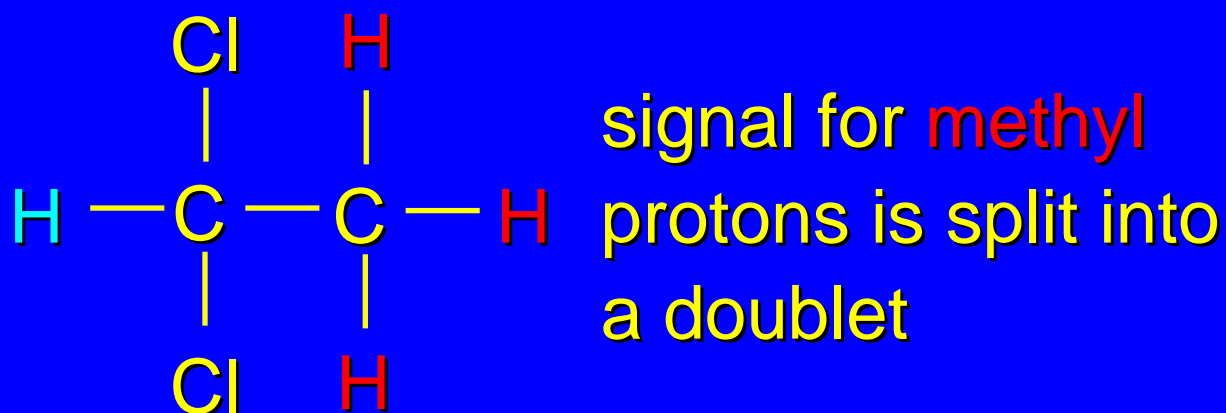
CH<sub>3</sub> splits CH into a quartet

*Why Do the Methyl Protons of  
1,1-Dichloroethane Appear as a Doublet?*



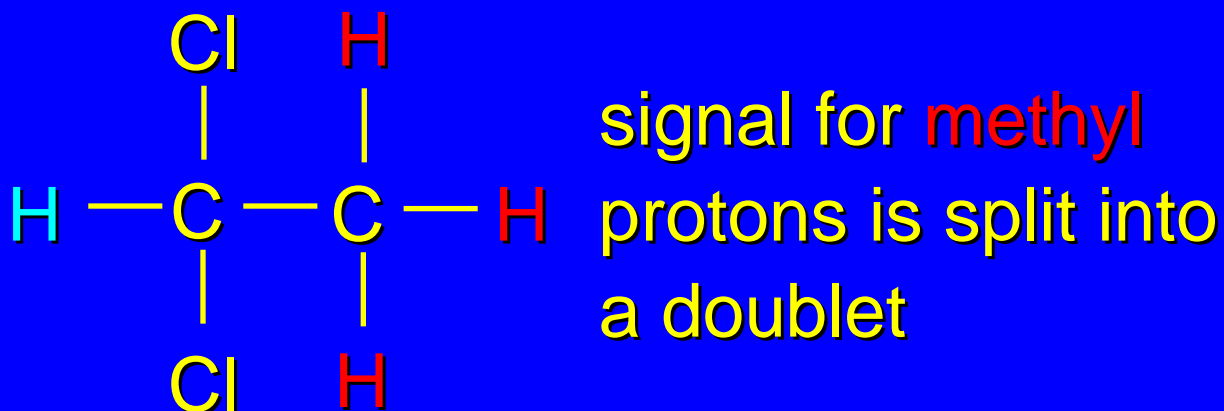
To explain the splitting of the protons at C-2, we first focus on the two possible spin orientations of the proton at C-1.

*Why Do the Methyl Protons of  
1,1-Dichloroethane Appear as a Doublet?*



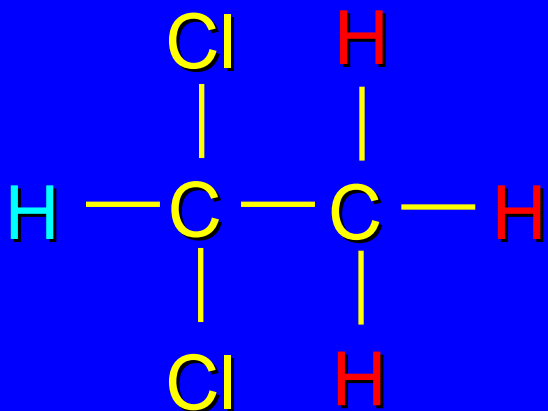
There are two orientations of the nuclear spin for the proton at C-1. One orientation shields the protons at C-2; the other deshields the C-2 protons.

*Why Do the Methyl Protons of  
1,1-Dichloroethane Appear as a Doublet?*



The protons at C-2 "feel" the effect of both the applied magnetic field and the local field resulting from the spin of the C-1 proton.

# Why Do the Methyl Protons of 1,1-Dichloroethane Appear as a Doublet?



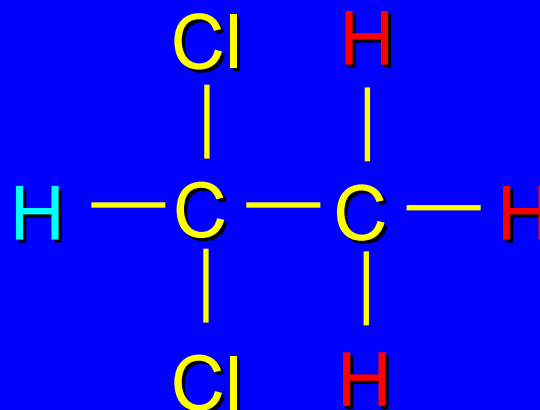
"true" chemical  
← shift of methyl  
protons (no coupling)

This line corresponds  
to molecules in which  
the nuclear spin of  
the proton at C-1  
*reinforces*  
the applied field.

This line corresponds  
to molecules in which  
the nuclear spin of  
the proton at C-1  
*opposes*  
the applied field.

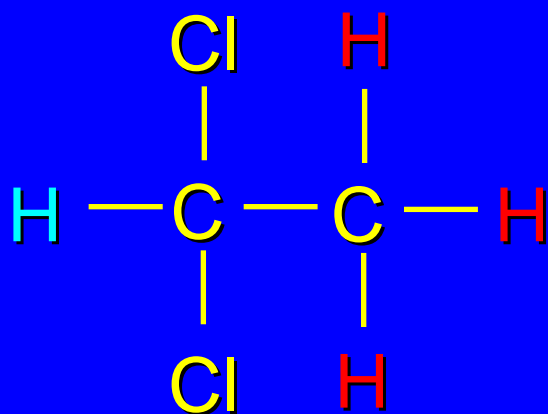
## Why Does the Methine Proton of 1,1-Dichloroethane Appear as a Quartet?

signal for methine proton is split into a quartet



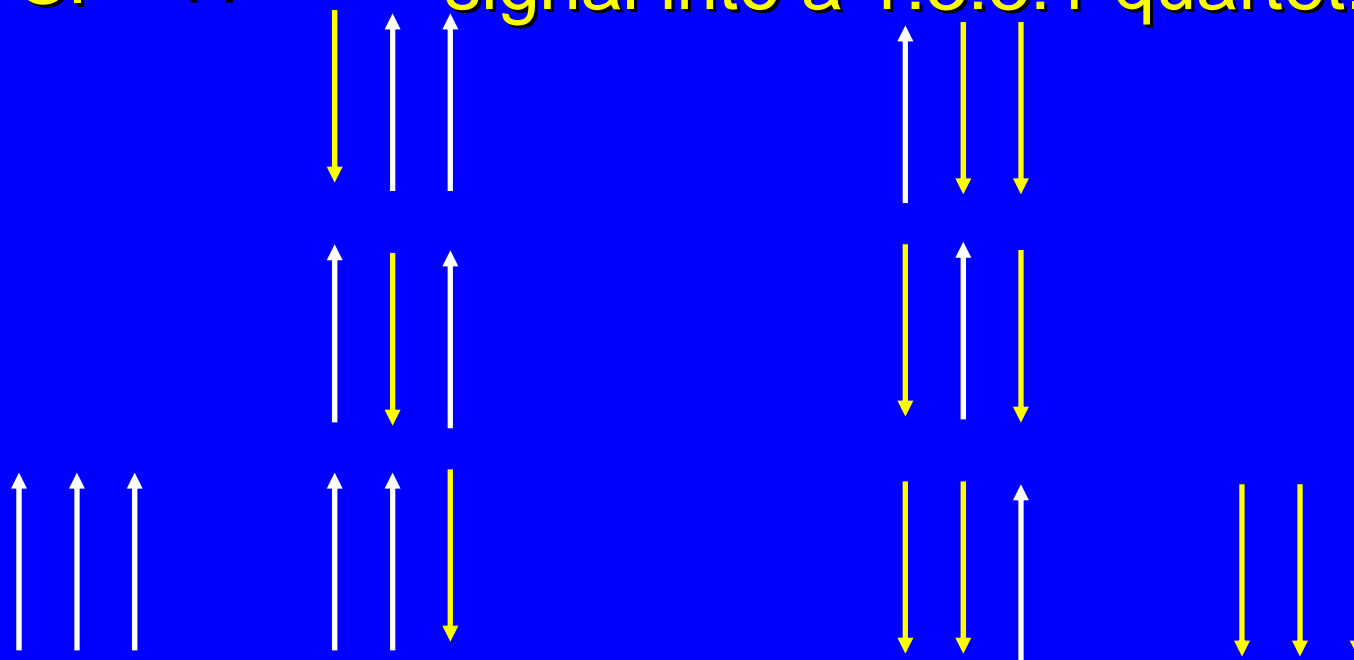
The proton at C-1 "feels" the effect of the applied magnetic field and the local fields resulting from the spin states of the three methyl protons. The possible combinations are shown on the next slide.

## Why Does the Methine Proton of 1,1-Dichloroethane Appear as a Quartet?



There are eight combinations of nuclear spins for the three methyl protons.

These 8 combinations split the signal into a 1:3:3:1 quartet.



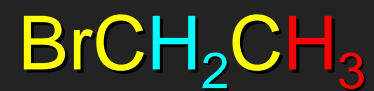
## *The Splitting Rule for $^1\text{H}$ NMR*

For simple cases, the multiplicity of a signal for a particular proton is equal to the number of equivalent vicinal protons + 1.

## Splitting Patterns: The Ethyl Group

$\text{CH}_3\text{CH}_2\text{X}$  is characterized by a triplet-quartet pattern (quartet at lower field than the triplet).

Figure 13.15

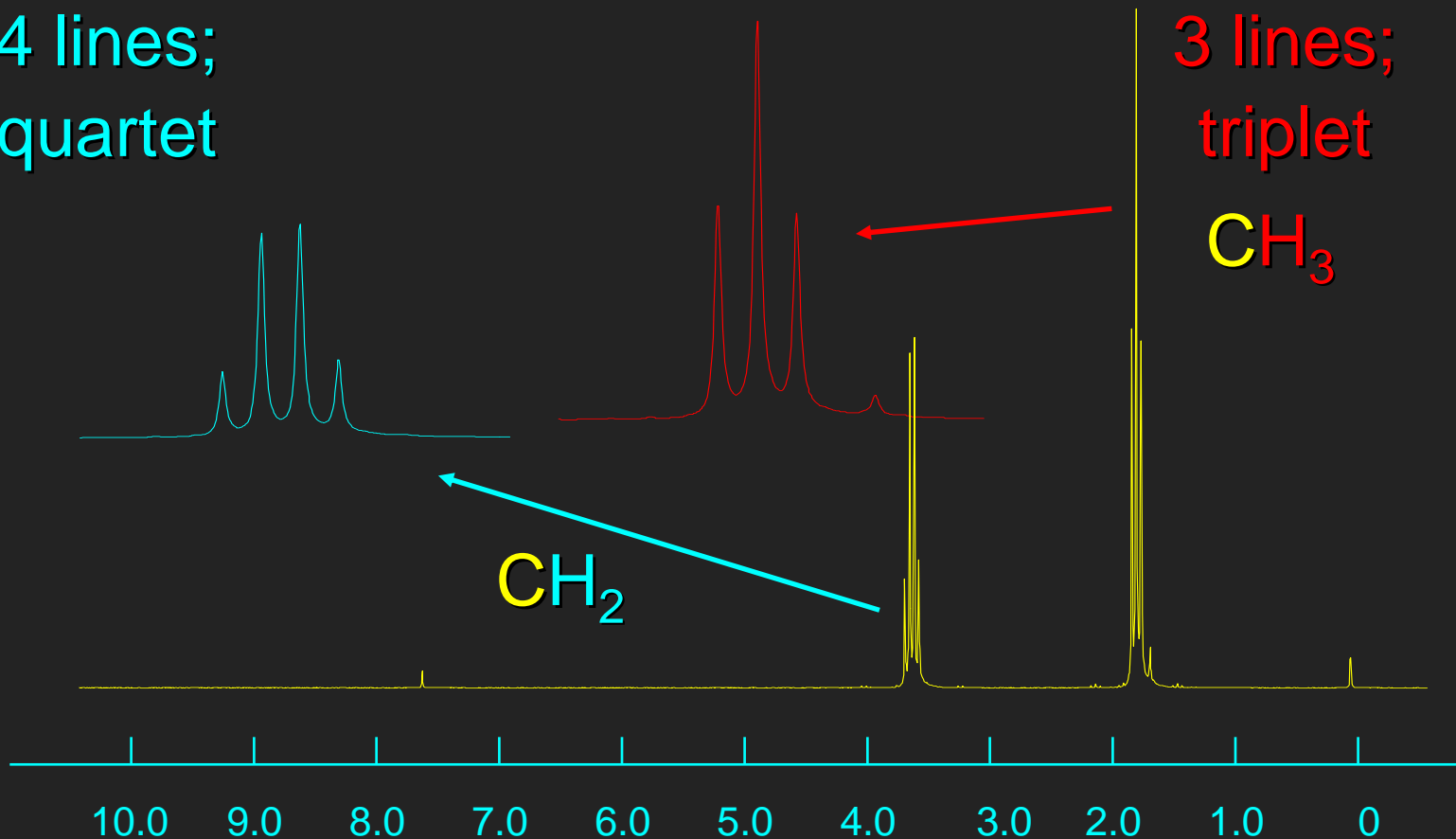


4 lines;  
quartet

3 lines;  
triplet

$\text{CH}_3$

$\text{CH}_2$



Chemical shift (δ, ppm)

*Table 13.2*

## Splitting Patterns of Common Multiplets

Number of equivalent protons to which H is coupled	Appearance of multiplet	Intensities of lines in multiplet
1	Doublet	1:1
2	Triplet	1:2:1
3	Quartet	1:3:3:1
4	Pentet	1:4:6:4:1
5	Sextet	1:5:10:10:5:1
6	Septet	1:6:15:20:15:6:1

## Splitting Patterns: The Isopropyl Group

$(\text{CH}_3)_2\text{CHX}$  is characterized by a doublet-septet pattern (septet at lower field than the doublet).

Figure 13.17

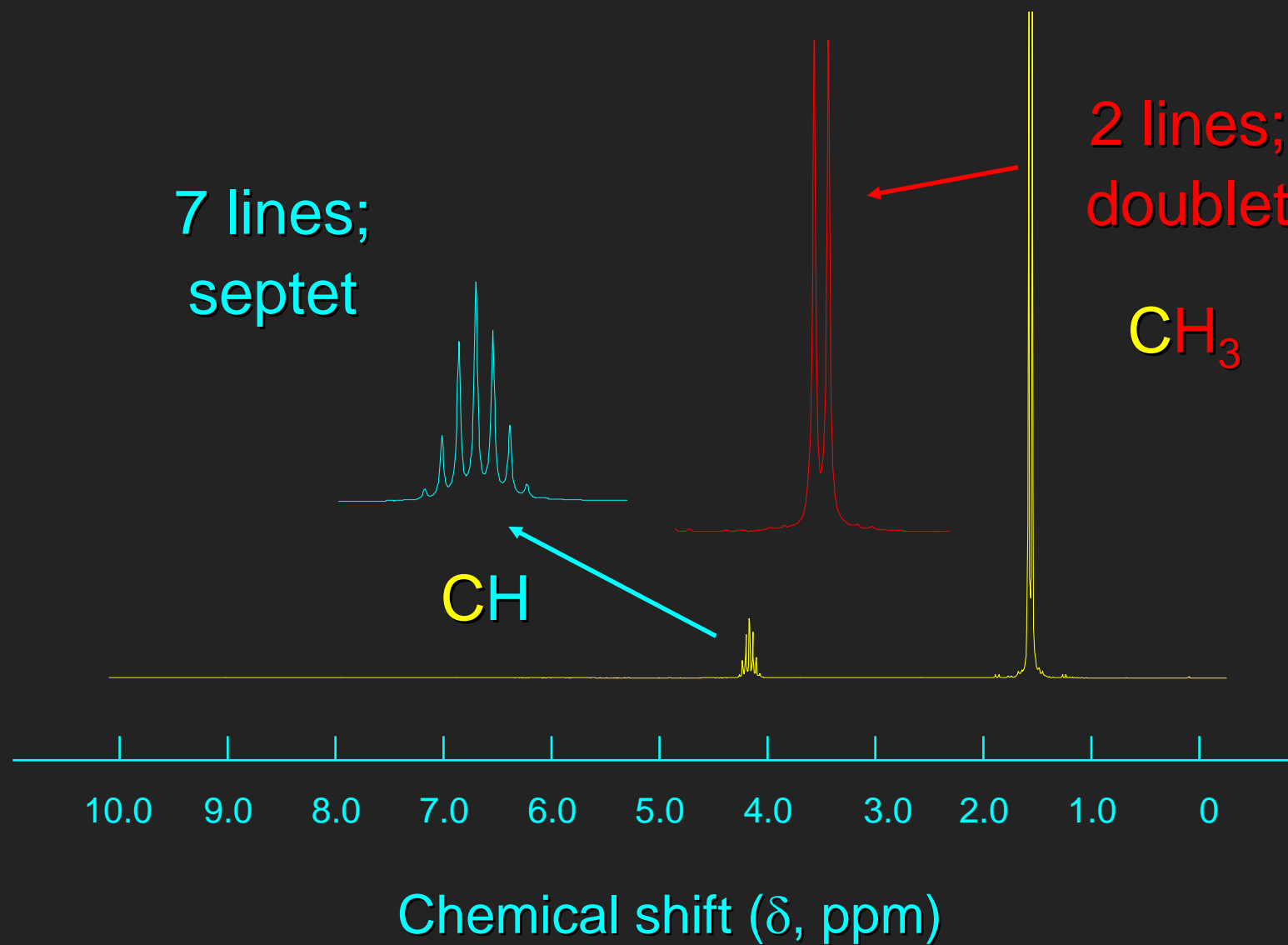
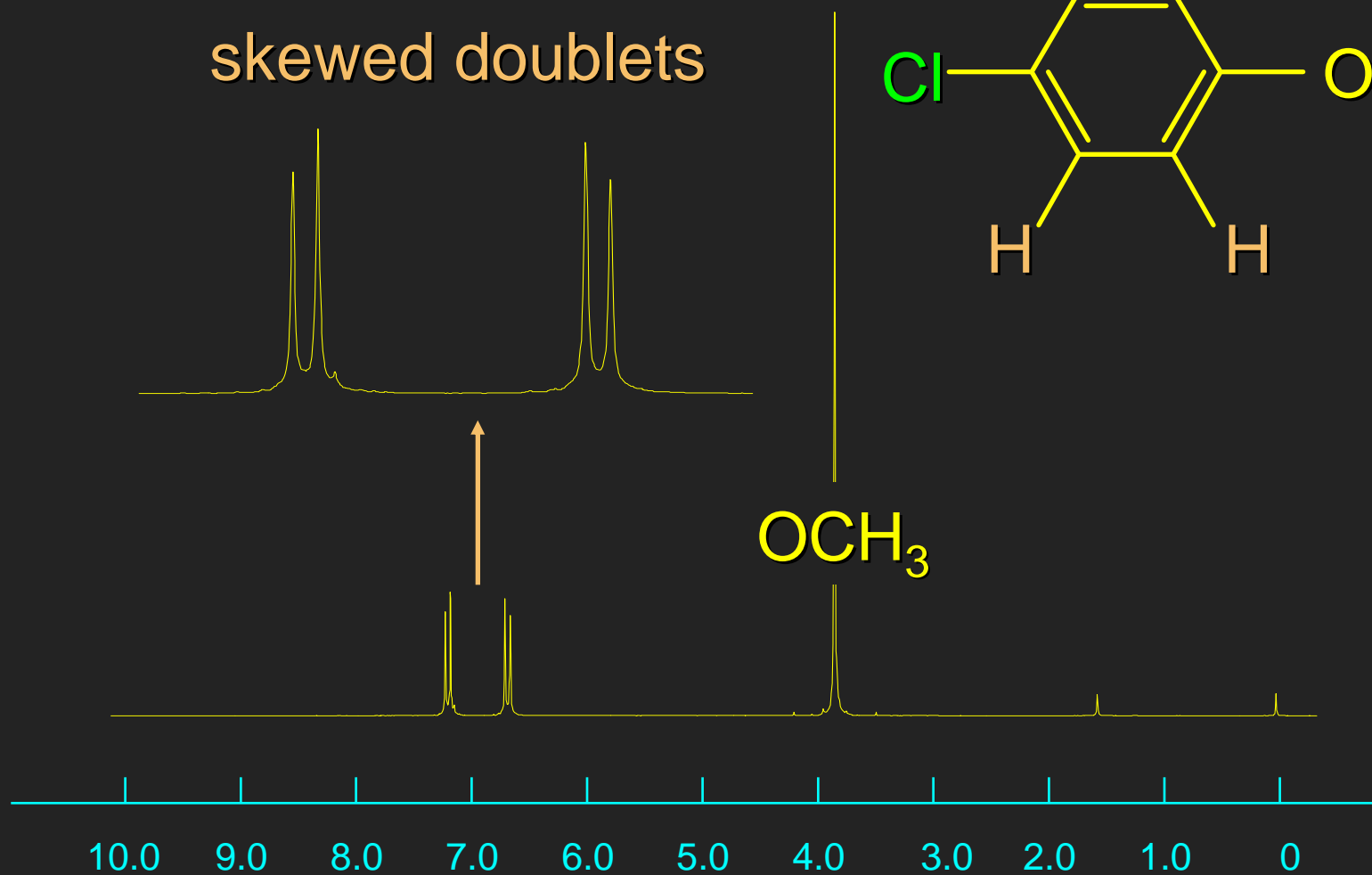
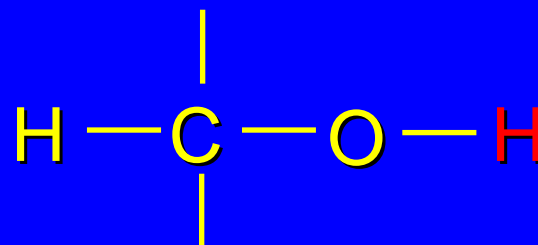


Figure 13.19

skewed doublets



Chemical shift ( $\delta$ , ppm)



The chemical shift for O—H is variable ( $\delta$  0.5-5 ppm) and depends on temperature and concentration.

Splitting of the O—H proton is sometimes observed, but often is not. It usually appears as a broad peak.

Adding  $\text{D}_2\text{O}$  converts O—H to O—D. The O—H peak disappears.