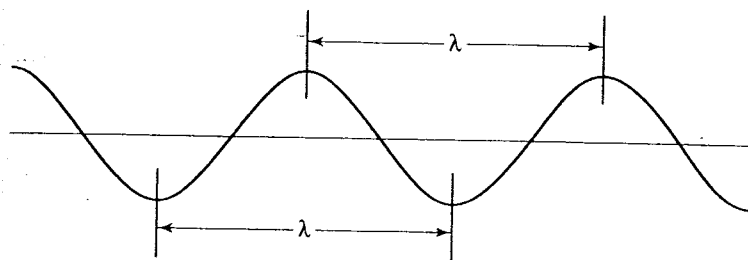


## CHAPTERS 13-15 SPECTROSCOPY

MUCH OF WHAT IS KNOWN ABOUT ORGANIC CHEMISTRY COMES FROM SPECTROSCOPY WHICH IS THE STUDY OF LIGHT, OR ELECTROMAGNETIC RADIATION (EM) AS IT INTERACTS WITH MATTER



The wavelength and frequency, which are inversely proportional, are related by equation

$$\nu\lambda = c \quad \text{or} \quad \lambda = \frac{c}{\nu}$$

$c$  = speed of light ( $3 \times 10^{10}$  cm/sec)

$\nu$  = frequency in hertz

$\lambda$  = wavelength in centimeters

INFRARED FREQUENCIES ARE ABOUT  $10^{14}$  Hz

IR SPECTRA ARE MEASURED IN % TRANSMITTANCE VS  $\text{cm}^{-1}$

IF A MOLECULE IS POLAR, ITS VIBRATING DIPOLES WILL ABSORB ENERGY WHEN THEY INTERACT WITH THE ELECTRIC FIELD OF EM AT RESONANCE

NO DIPOLE = NO IR ABSORPTION

STRETCHING FREQUENCIES DEPEND ON:

BOND STRENGTH			AND	ATOMIC MASS		
$\text{C}\equiv\text{C}$	$\text{C}=\text{C}$	$\text{C}-\text{C}$		$\text{C}-\text{H}$	$\text{C}-\text{D}$	$\text{C}-\text{C}$
2200	1660	1200		3000	2100	1200

## IMPORTANT STRETCHING FREQUENCIES ( $\text{cm}^{-1}$ )

C-C	1200	OF THESE, ONLY THE C=C IS COMMONLY USED
C=C	1660	
C≡C	2200	
		C≡C ISOLATED 1645
		C=C CONJUGATED 1620
		AROMATIC 1600

## C-H STRETCHING

$sp^3$  LESS THAN 3000 (TO THE RIGHT OF 3000)

$sp^2$  GREATER THAN 3000 (TO THE LEFT OF 3000)

$sp$  3300

## ALCOHOLS AND AMINES

R-OH 3300, BROAD

R-N-H 3300, BROAD, WITH SPIKES (1 FOR  $2^\circ$ )  
(2 FOR  $1^\circ$ )

R-C(=O)-OH 3000, BROAD

## CARBONYLS - A VERY STRONG PEAK

ENTERED AT 1710

ALDEHYDES ARE DISTINGUISHED BY 2 C-H STRETCHES AT 2700, 2800

ACIDS ARE DISTINGUISHED BY BROAD OH, 3000

CONJUGATION LOWERS THE C=O STRETCH TO THE 1680 REGION

AMIDES ARE THE LOWEST FREQUENCIES, 1630-1650

VS C=C, AMIDES HAVE NO  $sp^2$  C-H ( $>3000$ ) AND SHOW

STRONG, BROAD N-H 3000-3500

A FEW CARBONYLS ABSORB HIGHER THAN 1710

ESTERS  $\rightarrow \approx 1735$

TRAINED RING KETONES  $\rightarrow$  TO 1790

-N BONDS ABSORB MORE STRONGLY THAN C-C BONDS (MORE POLAR)

C=N  $\approx 1660$

C≡N 2200 VERY STRONG AND SHARP

## MASS SPECTROMETRY

MOLECULES ARE FRAGMENTED BY ELECTRON IMPACT (ONE OF MANY TECHNIQUE)

THE FRAGMENTS ARE MASS ANALYZED

STRONGEST PEAK IS THE BASE PEAK

MOLECULAR ION IS CALLED THE PARENT PEAK = MOLECULAR WEIGHT = "M"

VERY HIGH RESOLUTION MASS SPECTROMETERS CAN GIVE "EXACT" MASS

FROM WHICH A UNIQUE MOLECULAR FORMULA IS OBTAINED

$M+1 = \text{PARENT} + 1$   
 $M+2 = \text{PARENT} + 2$  } COME FROM HEAVIER ISOTOPES

THIS LEADS TO A FEW RECOGNIZABLE PATTERNS

B<sub>2</sub>  $M+2 = 100\%$  OF  $M$

Cl  $M+2 = 33\%$  OF  $M$

I  $I^+ = 127$ , LARGE GAP

N ODD  $M$

S  $M+2$  SLIGHTLY LARGER (4% OF  $M$ )

FRAGMENTATION PATTERNS

ALMOST ALL POSSIBLE FRAGMENTS ARE CREATED, BUT THERE ARE A FEW ESPECIALLY STABLE ONES

THESE ARE OFTEN HIGHLY STABLE CATIONS: ALLYL, BENZYL ( $3^\circ$ ,  $2^\circ$ )

ALCOHOLS LOSE  $H_2O$ , LOOK FOR AN  $M-18$  PEAK (EVEN#)

SKILLS

IDENTIFY COMMON IR PEAKS

EXPLAIN WHY PEAKS ARE STRONG, WEAK, OR ABSENT

IDENTIFY THE VARIOUS CARBONYL PEAKS (CONJUGATION)

IDENTIFY THE C=C PEAKS (CONJUGATION)

USE MS FOR MW

USE MS FOR B<sub>2</sub>, Cl, S, I, N

IDENTIFY FRAGMENTATION PATTERNS

AND USE FOR STRUCTURE

PROBLEMS

3, 4, 16, 19A, 25

2, 14

31, 5, 52, 6

14, 15

7, 20

8, 9, 10, , 11

180

TABLE 12-2 SUMMARY OF IR ABSORPTION FREQUENCIES

Frequency ( $\text{cm}^{-1}$ )	Functional Group	Comments	
3300	alcohol amine, amide alkyne	$\text{O}-\text{H}$ $\text{N}-\text{H}$ $\equiv\text{C}-\text{H}$	always broad may be broad, sharp, or broad with spikes always sharp, usually strong
3000	alkane	$\begin{array}{c}   \\ -\text{C}-\text{H} \\   \end{array}$	just below $3000 \text{ cm}^{-1}$
	alkene	$\begin{array}{c} \text{H} \\ \diagup \\ =\text{C} \\ \diagdown \end{array}$	just above $3000 \text{ cm}^{-1}$
	acid	$\text{O}-\text{H}$	very broad
2200	alkyne nitrile	$-\text{C}\equiv\text{C}-$ $-\text{C}\equiv\text{N}$	just below $2200 \text{ cm}^{-1}$ just above $2200 \text{ cm}^{-1}$
1710 (very strong)	carbonyl	$\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$	ketones, aldehydes, acids esters higher, about $1735 \text{ cm}^{-1}$ conjugation lowers frequency amides lower, about $1650 \text{ cm}^{-1}$
1660	alkene	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$	conjugation lowers frequency aromatic $\text{C}=\text{C}$ about $1600 \text{ cm}^{-1}$
	imine	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{N} \\ \diagdown \quad \diagup \end{array}$	stronger than $\text{C}=\text{C}$
	amide	$\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$	stronger than $\text{C}=\text{C}$ (see above)

Ethers, esters, and alcohols also show  $\text{C}-\text{O}$  stretching between  $1000$  and  $1200 \text{ cm}^{-1}$ .

**ALDEHYDE 2700 + 2800**

CHAPTER 14 LECTURE NOTES FOR ORGANIC CHEMISTRY © MM 2001  
INTERPRETATION OF NMR SPECTRA 2006

MANY NUCLIDES ARE MAGNETIC:  $^1\text{H}$  AND  $^{13}\text{C}$  HAVE MAGNETIC NUCLEI. WHEN A SAMPLE IS PLACED IN A STRONG MAGNETIC FIELD ( $B_0$ ) THESE NUCLEI ACT AS LITTLE BAR MAGNETS

A NUCLEUS ALIGNED IN THE SAME DIRECTION AS  $B_0$  IS IN A LOW ENERGY STATE, LIKE A COMPASS POINTING NORTH

A NUCLEUS ALIGNED IN THE OPPOSITE DIRECTION IS IN A HIGH ENERGY STATE. NMR SPECTROSCOPY OBSERVES TRANSITIONS BETWEEN THESE TWO ENERGY STATES.

THE PHOTON THAT IS ABSORBED IS OF VERY LOW ENERGY, WITH A FREQUENCY IN THE MEGAHERTZ RANGE ( $10^6 \text{ Hz}$ , OR  $10^6$  CYCLES PER SECOND)

THIS IS A TYPE OF ABSORPTION/EMISSION SPECTROSCOPY, THE NUCLEI ARE PUT INTO THE HIGHER ENERGY STATE BY ABSORBING A PHOTON. AS THE NUCLEI RETURN TO THE LOWER ENERGY STATE THEY EMIT A PHOTON THAT IS THE NMR SIGNAL

THE ONE CRUCIAL IDEA: FREQUENCY OF THE NMR SIGNAL DEPENDS ON THE MAGNETIC FIELD STRENGTH ( $B_0$ )

THIS IS EXPRESSED BY THE LARMOR EQUATION  $\omega = \gamma B_0$

FREQUENCY ( $\omega$ ) = MAGNETOGYRIC RATIO  $\times$  FIELD STRENGTH ( $\gamma \times B_0$ )

THE MAGNETOGYRIC RATIO IS UNIQUE FOR EACH ISOTOPE

THIS MEANS THAT ALL PROTONS HAVE THE "SAME" FREQUENCY IN A GIVEN FIELD STRENGTH (AS IN MRI, MAGNETIC RESONANCE IMAGING)

FORTUNATELY, EACH PROTON IN A MOLECULE FINDS ITSELF IN A SLIGHTLY DIFFERENT MAGNETIC ENVIRONMENT, DUE TO AN EFFECT CALLED SHIELDING.

ELECTRONS IN BONDS PRODUCE MAGNETIC FIELDS THAT EITHER OPPOSE  $B_0$  (SHIELD) OR REINFORCE  $B_0$  (DESHIELD)

SO THE EFFECTIVE MAGNETIC FIELD STRENGTH IS SLIGHTLY DIFFERENT FOR DIFFERENT TYPES OF PROTONS (ONLY A FEW PARTS PER MILLION, PPM) THIS IS CALLED CHEMICAL SHIFT

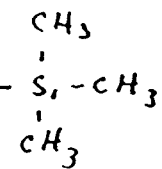
FROM EACH PROTON SPECTRUM WE WILL GET 4 PIECES OF INFORMATION:

- 1) HOW MANY SIGNALS = HOW MANY DIFFERENT TYPES OF PROTONS
- 2) HOW STRONG ARE THE SIGNALS (INTEGRATION)  
TELLS HOW MANY PROTONS OF EACH TYPE
- 3) CHEMICAL SHIFT OF EACH SIGNAL  
TELLS WHICH TYPES OF FUNCTIONAL GROUP IS PRESENT
- 4) SPLITTING PATTERN  
TELLS HOW MANY NEIGHBORING PROTONS ARE PRESENT

# CHEMICAL SHIFT

- EXPRESSED IN PPM

- REFERENCED TO TETRAMETHYL SILANE (TMS) = 0



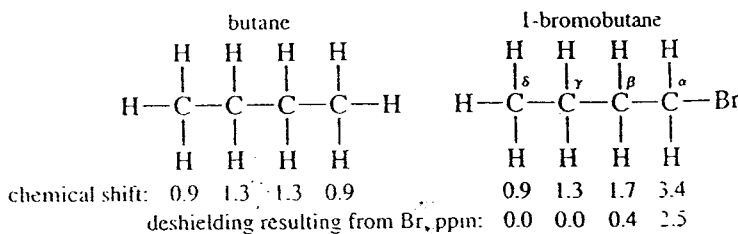
- DUE TO SHIELDING

ELECTRONS IN  $\sigma$  BONDS "SHIELD" THE NUCLEUS FROM  $B_0$ , PRODUCE A LOWER EFFECTIVE FIELD AND LOWER FREQUENCY, LOWER CHEMICAL SHIFT, IF ELECTRONS SHIELD, ELECTRON WITHDRAWING GROUPS "DESHIELD" PRODUCING HIGHER FREQUENCIES, HIGHER CHEMICAL SHIFTS.

TABLE 13-1 Variation of Chemical Shift with Electronegativity

	X in $\text{CH}_3\text{-X}$				
	F	OH	Cl	Br	I
electronegativity of X	4.0	3.4	3.2	3.0	2.7
chemical shift of $\text{CH}_3\text{-X}$	84.3	83.4	83.0	82.7	82.2

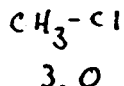
## THE EFFECT DIMINISHES WITH DISTANCE



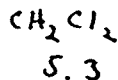
## THE EFFECT IS ADDITIVE (APPROXIMATELY)



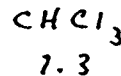
+2.8



+2.3



+2



VINYLS AND AROMATIC PROTONS ARE ESPECIALLY DESHIELDED BY A MAGNETIC FIELD PRODUCED BY  $\pi$  ELECTRONS

VINYL  $\rightarrow$  5-6 ppm

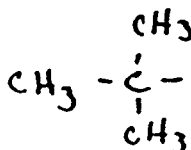
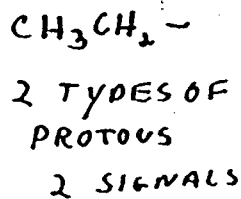
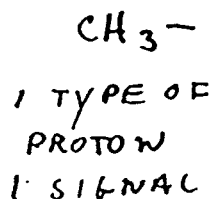
AROMATIC 6-8 ppm

ALDEHYDE PROTONS EXPERIENCE SIMILAR  $\pi$ -DESHIELDING PLUS INDUCTIVE EFFECT OF  $\text{C=O} \rightarrow$  9-10 ppm

CARBOXYLIC ACID PROTONS  $\rightarrow$  10+ ppm

## THE NUMBER OF NMR SIGNALS

PROTONS IN IDENTICAL CHEMICAL ENVIRONMENTS WITH THE SAME SHIELDING ARE CALLED CHEMICALLY EQUIVALENT ONLY 1 SIGNAL IS SEEN FOR "EQUIVALENT" PROTONS



1 TYPE OF PROTON  
1 SIGNAL

## THE STRENGTH OF THE NMR SIGNAL

THE AREA UNDER A PEAK IS PROPORTIONAL TO THE NUMBER OF PROTONS

INTEGRATED AREAS WILL BE PROVIDED FOR ALL NMR PEAKS IN THIS COURSE

SOMETIMES THE AREAS WILL BE ABSOLUTE (AS IN "EQUALS 2 PROTONS")

SOMETIMES RELATIVE (AS IN 3:1 RATIO OF AREAS)

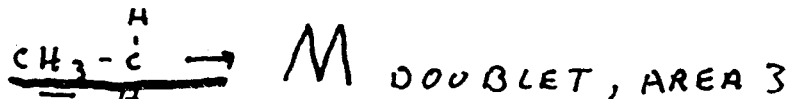
## THE SPIN-SPIN SPLITTING PATTERN

DUE TO AN EFFECT CALLED "COUPLING"

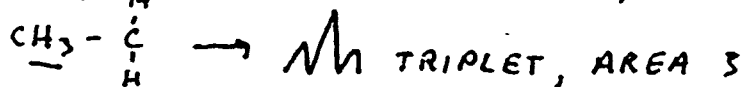
LEADING TO THE  $n+1$  RULE

IF A SIGNAL IS SPLIT BY  $n$  EQUIVALENT PROTONS, IT GIVES  $n+1$  PEAKS

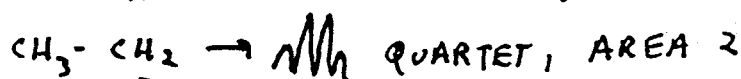
SO, 1 NEIGHBORING PROTON



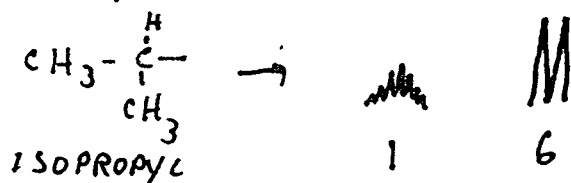
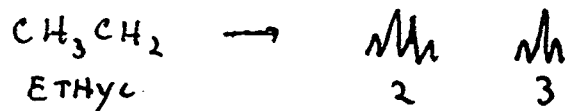
2 NEIGHBORING PROTONS



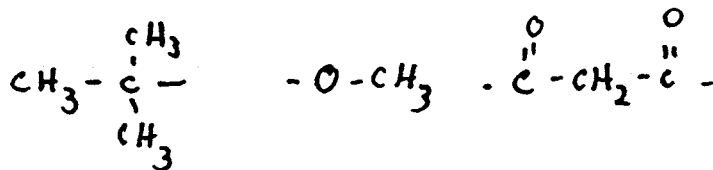
3 NEIGHBORING PROTONS



## SOME VERY COMMON PATTERNS



SINGLET MEAN NO NEIGHBORS



## THE RANGE OF COUPLING

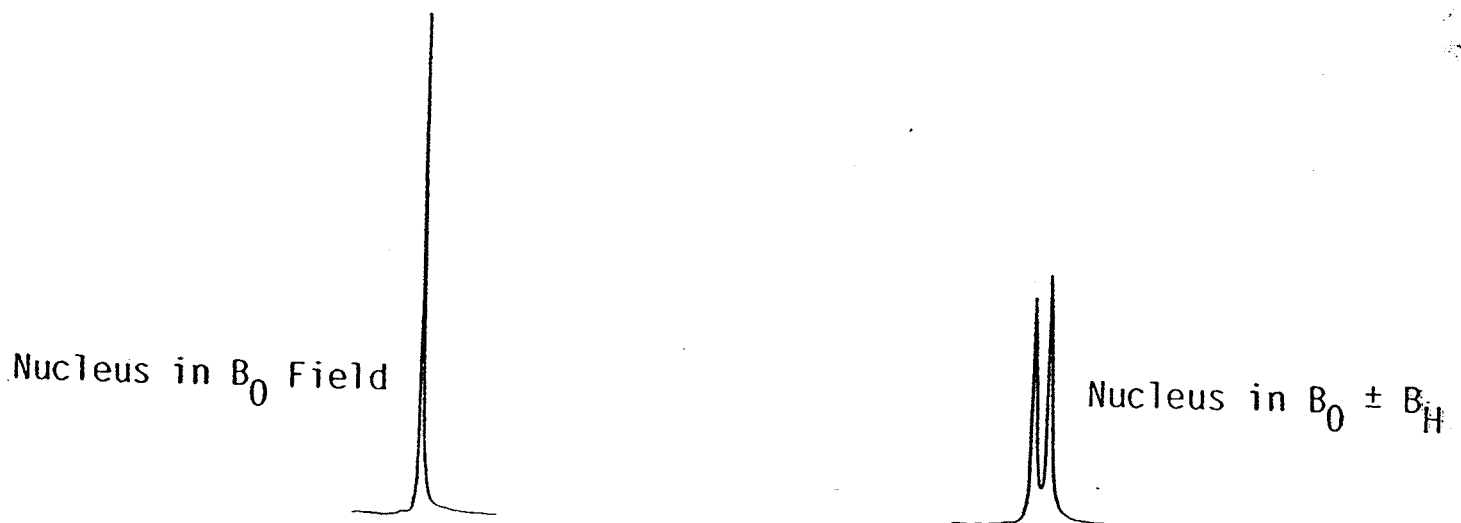
- USUALLY RESTRICTED TO 3 BONDS

- 4 AND 5 BOND COUPLING MAY BE SEEN, ESPECIALLY IN  $\pi$  SYSTEMS

## COUPLING

A SINGLE RESONANCE LINE IS DECOMPOSED INTO TWO LINES BY COUPLING WITH A NEIGHBORING NUCLEUS

THIS IS BECAUSE THE RESONANCE LINE EXPERIENCES TWO DIFFERENT FIELD STRENGTHS, ONE HIGHER THAN  $B_0$  AND ONE LOWER, DUE TO THE TWO POPULATIONS OF THE NEIGHBORING NUCLEUS -- ALIGNED EITHER WITH OR AGAINST  $B_0$



### POINTS TO REMEMBER

- THE STRENGTH OF THE INTERACTION BETWEEN COUPLED NUCLEI IS EXPRESSED IN Hz AND IS NAMED J
- THE EFFECT IS TRANSMITTED THROUGH CHEMICAL BONDS AND DECREASES AS THE NUMBER OF BONDS BETWEEN ATOMS INCREASES
- THE COUPLING CONSTANT IS INDEPENDENT OF EXTERNAL FIELD STRENGTH



## CARBON-13 SPECTRA

WE WILL TREAT THEM ALMOST THE SAME AS  $^1\text{H}$  SPECTRA

EXCEPT:

- THE CHEMICAL SHIFT IS LARGER, MORE THAN 200 ppm
- THE SPECTRA ARE NOT USUALLY INTEGRATED
- FOR NOW, WE WILL NOT LOOK AT COUPLING PATTERNS

THIS LEAVES US WITH:

1) THE NUMBER OF SIGNALS

- REFLECTS THE NUMBER OF DIFFERENT TYPES OF CARBONS

2) THE CHEMICAL SHIFTS

- USING THE USUAL ELECTRONEGATIVITY AND  $\pi$  SHIELDING REASONING

SIMILAR TO  $^1\text{H}$

$\text{CH}_4$	$\text{CH}_3\text{Cl}$	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$	$\text{CCl}_4$
-22.0	25	54	77	97
	+27	+29	+23	+20

HOWEVER, THIS TREND DOES NOT HOLD FOR BROMIDES AND IODIDES

ALKENES AND AROMATICS STRONGLY DESHIELDED

ALKENES 100-150

AROMATICS 120-148 BENZENE = 128

ALKANES - SHIELDED  $\rightarrow \approx 20$

$\text{C}=\text{O} \rightarrow 50-60$

$\text{C}=\text{C} \rightarrow 160-190$

$\text{R}-\overset{\text{||}}{\text{C}}-\text{R} > 180$

$\text{C}-\text{X}$ , HALOGENS  $\approx 20-40$

$\text{C}-\text{N} \approx 30-50$

SKILL	PROBLEMS
PREDICT IR BANDS	13, 15, 26, 27, 28
DETERMINE FUNCTIONAL GROUPS FREQUENCY, MASS, BOND STRENGTH	14, 16, 17, 18
PREDICT NMR SPECTRA, SHIFTS, INTEGRALS, COUPLING	15, 16, 30
DETERMINE STRUCTURES FROM SPECTRA	18, 19, 20
USE COMBINED IR, NMR	21, 22
PREDICT THE MASS SPECTRUM OF A COMPOUND	18, 19
EXPLAIN FRAGMENTATION PATTERNS	20, 21
IDENTIFY B <sub>2</sub> + C <sub>1</sub> ISOTOPIC SIGNATURES	23, 27
CONJUGATION AND UV SPECTRA	6, 17 (CHAPTER 15)