Name: _____ Date: _____ Period: _____

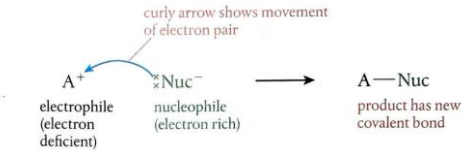
HL Topic 10 Organic Chemistry - Guided Notes

Slide 3: You Try!

- What types of reactants undergo these reactions:
- nucleophilic substitution
- electrophilic addition
- electrophilic substitution

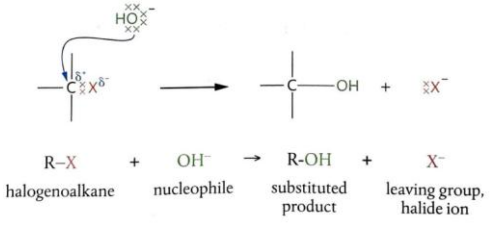
Slide 4: Curly arrow represents motion of electron pair.
Tail shows where electron comes from and head of arrow shows where it is going.

- How To Show _____ Movement



Slide 5: Halogenoalkanes have a polar carbon-hydrogen bond.
Makes carbon atom electron-deficient and susceptible to nucleophilic attack
Carbon-halogen bond breaks and the halogen is released as a halide (negative ion).
Halogen is called the leaving group because it is removed from the halogenoalkane

- _____ Substitution (S_N) Reactions
- **bond breakage where both shared _____ go to one of the products**
- **Heterolytic fission**
- X _____ any halogen
- _____ fission of the C-X bond occurs

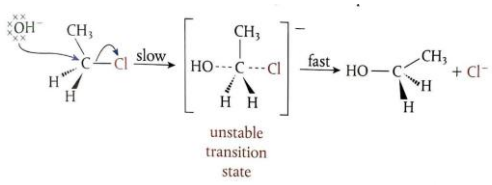


Slide 6: Nucleophilic substitution reactions are categorized based on their rates.
SN1 reactions are first-order (depend only on concentration of the substrate.
SN2 reactions are second- order (depend on concentration of substrate and nucleophile).

- S_N1 vs. S_N2 _____

Slide 7: One-step reactions that have an unstable transition state
Bimolecular reaction (second-order)
Strong nucleophile attacks electrophilic carbon atom on opposite side from the leaving group
Occur fastest with primary halogenoalkanes

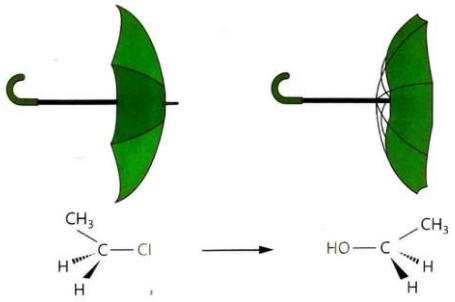
- S_N2 Reactions



$$C_2H_5Cl + OH^- \rightarrow C_2H_5OH + Cl^-$$

Slide 8: Inversion of the atom arrangement occurs around the carbon atom occurs due to position of nucleophilic attack.

- S_N2 Reactions



Slide 9: SN2 reactions are stereospecific

Due to the fact that bond formation comes before bond cleavage in the transition state, so stereochemistry of the carbon attacked is preserved.
Stereochemistry important in synthesis of biological molecules (e.g. amino acids, pharmaceuticals, etc.)

- S_N2 Reactions
- 3-D _____ of reactants determines the 3-D arrangement of products.

Slide 10: Favored by polar, aprotic solvents

Aprotic solvents solvate the metal cation, which allows the nucleophile to be separated (higher energy state) and increases the reaction rate.
Include propanone ((CH3)2CO), methylene chloride (CH2Cl2), and ethanenitrile (CH3CN).

- S_N2 Reactions
- Don't have -OH or -NH bond so don't form _____ bonds. Also contain strong dipoles

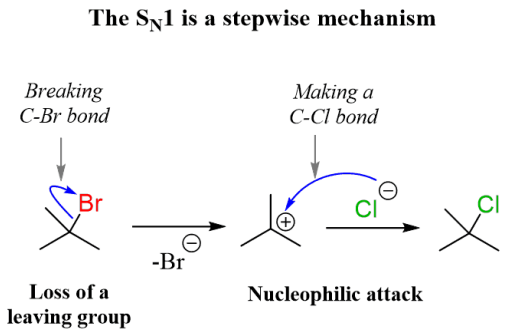
Slide 11: You Try!

- Draw the reaction mechanism for the following:
- bromomethane in sodium hydroxide
- 1-bromopropane in potassium cyanide
- 2-chlorobutane in potassium hydroxide

Slide 12: Two-step reactions that have a carbocation intermediate
Unimolecular reaction (first-order)
Weak nucleophile attacks electrophilic carbon atom on either side of the carbocation (2 products possible)
Occur fastest with tertiary halogenoalkanes

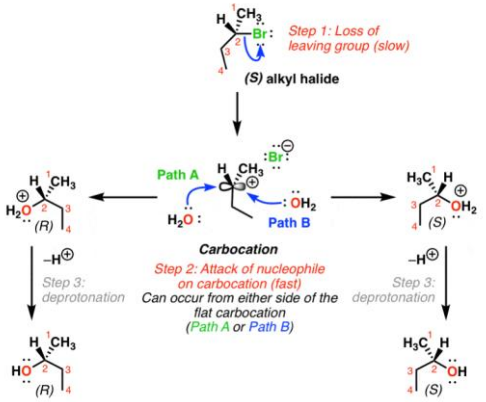
- S_N1 Reactions

- **Steric hindrance** (bulky alkyl groups) of tertiary alkanes prevent direct attack from _____ via S_N2 mechanism
- The three alkyl groups stabilize the _____ because each one has a **positive inductive** (electron-donating) effect



Slide 13: SN1 Reactions

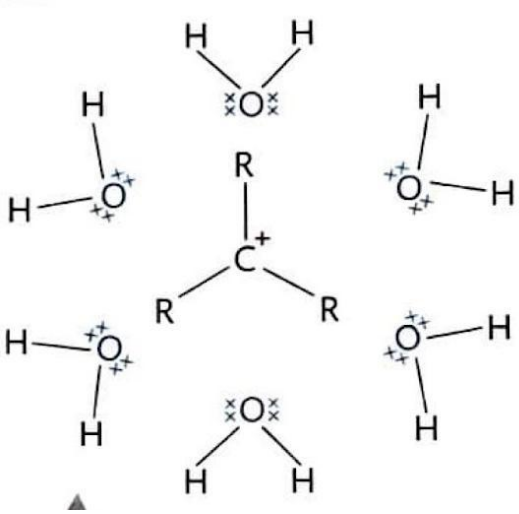
- **S_N1 reactions are NOT _____**
- **The _____ inductive effect allows carbocation to remain long enough for second step to occur.**



Slide 14: Favored by polar, protic solvents

Protic solvents stabilize the carbocation intermediate through ion-dipole interactions.
Include water, alcohols, and carboxylic acids.

- S_N1 Reactions
- Contain -OH or -NH bond so DO form _____ bonds.



Slide 15: Undergo both SN1 and SN2 reactions

Can't be precise about mechanism of nucleophilic substitution.

- Secondary _____

Slide 16: You Try!

- Draw the reaction mechanism for the following:
- 2-bromo-2-methylbutane in ethanol
- 3-chloro-3-methylhexane in water
- 2-bromo-2-methylpropane in methanoic acid

Slide 18: Rates of Nucleophilic Substitution Rxns

- Factors that affect _____ rates:
- Mechanism of Rxn
- Leaving group
- Solvent

Slide 19: Rates: Mechanism of Rxn

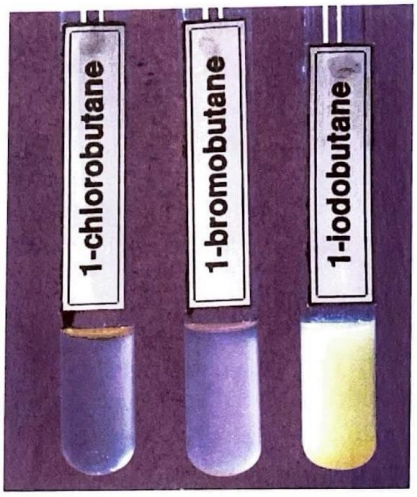
- S_N1 _____ proceed more quickly than S_N2
- This is due to the ability of protic solvents to stabilize the carbocation _____ in S_N1 reactions.

tertiary	>	secondary	>	primary
S_N1		S_N1 and S_N2		S_N2

Slide 20: Rates: Leaving Group

- As _____ of halogen decreases (going down the group), the carbon in the carbon-halogen bond becomes **less** electron-deficient, so less vulnerable to nucleophilic attack.
- However, the **strength** of the carbon-halogen bond _____ in strength going down the group, so bonds are more easily broken.
- **_____ with silver nitrate in alcoholic solution**

iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes



Slide 21: Rates: Solvent

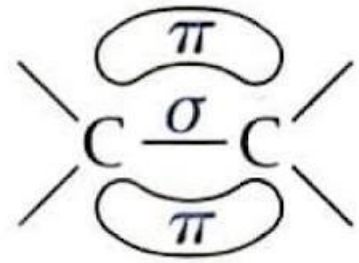
- S_N1 mechanism favored by polar, protic solvents
- S_N2 mechanism favored by polar, aprotic solvents
- To track rate of nucleophilic substitution reactions, silver nitrate can be added and the precipitate of the silver halide can be observed (each has a distinct color)
- What are the conditions that would produce the fastest nucleophilic substitution reactions? If you were to observe the rate of this reaction with silver nitrate, what would you see?

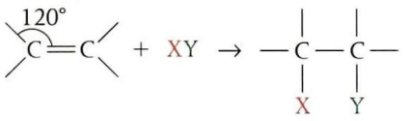
Slide 23: Alkenes susceptible to electrophilic addition reactions due to nature of C-C double bond Examples: addition of halogens and hydrogen halides to alkenes (occur under mild conditions). Electrophile produced through heterolytic fission

- Electrophilic Addition Reactions
- **pi bond above and below the plane of the bond axis (weaker and more easily broken)**
- *carbon atoms of double bond are sp^2 hybridized
- *trigonal planar geometry is open structure that makes it easy for

incoming electrophilic attack

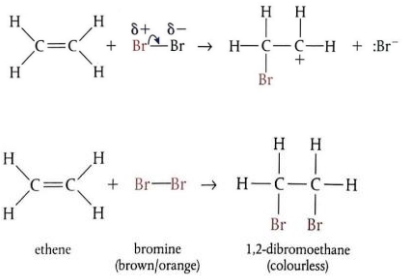
- *reactants attach at each carbon atom once double bond is broken
- **pi bond attractive to electrophiles due to electron density**

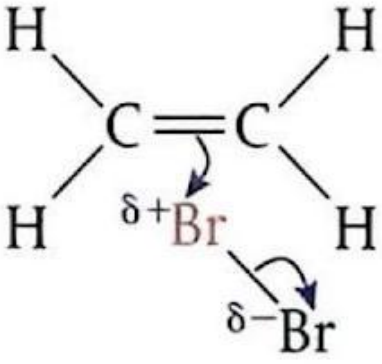


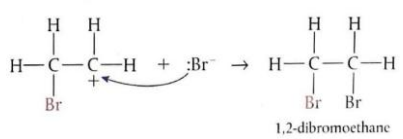


Slide 24: Electrophilic Addition Reaction: Ethene + Br2

- **Ethene bubbled through bromine (brown) at room temp. produces 1,2-_____ (colorless)**
- **Br_2 _____ e^- rich region and becomes polarized**
- **Br_2 is _____ cleaved, Br^+ attacks the alkene, breaking the pi bond (slow step). An unstable carbocation intermediate is formed.**
- **Br^- reacts with carbocation _____ to form product (fast step)**
- **1.**
- **2.**





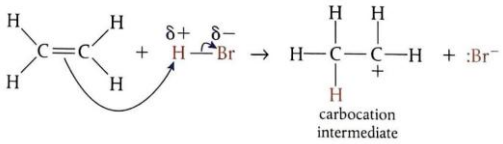


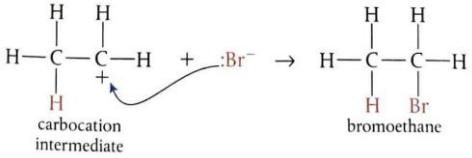
Slide 25: Explain why BrH2CCH2Br and BrH2CCH2Cl are formed from the reaction of ethene with Br2 and Cl- ions.

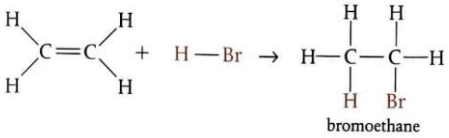
- Evidence for _____ Addition Reactions

Slide 26: Electrophilic Addition Reaction: Ethene + HBr

- **Ethene bubbled through _____ HBr at room temp. produces bromoethane**
- **HBr undergoes heterolytic fission to form H^+ and Br^-. The _____ (H^+) attacks double bond to form unstable carbocation.**
- **Carbocation _____ reacts quickly with Br^- to form product.**
- **1.**
- **2.**

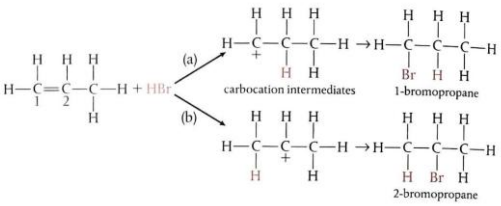






Slide 27: Electrophilic Addition Reaction: Propene + HBr

- **Propene is an unsymmetric alkene, so _____, two different products can form upon addition with a hydrogen halide. This depends on which carbon to which the electrophile bonds.**

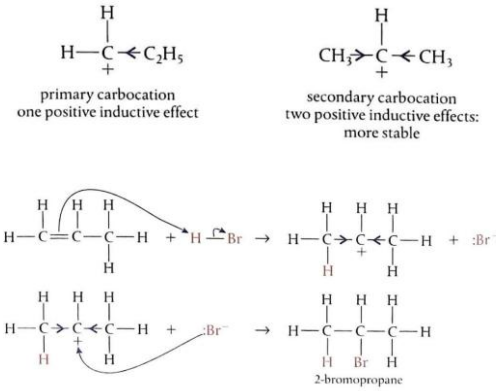


Slide 28: Electrophilic Addition Reaction: Propene + HBr

- **Pathway (a) forms a primary _____. Pathway (b) forms a secondary carbocation. The secondary carbocation is more stable due the greater positive**

inductive effect.

- **2-_____ is main product formed (called the "major" product)**



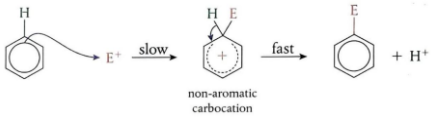
Slide 29: Markovnikov's Rule

- **The more _____ part of the reacting species bonds to the least highly substituted carbon atom in the alkene**
- **The hydrogen will attach to the carbon that is already bonded to the greater number of _____**
- **The _____ will form on the carbon bonded to more carbon atoms.**
- In technical terms:
- In general terms:
- **Note: When asked to predict major products of an _____ addition reaction, you MUST mention carbocation stability due to inductive effects.**

Slide 30: You Try!

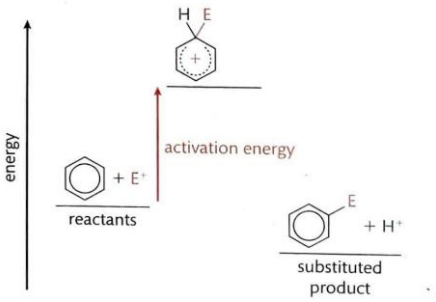
- Write names and structures for the two possible products of the addition of the interhalogen compound BrCl to propene. Consider which is likely to be the major product and explain why.

Slide 31: Electrophilic Substitution Reactions: Benzene



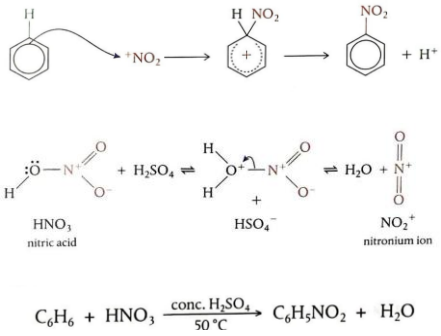
- **Although unsaturated, benzene has a stable aromatic ring, favoring _____ reactions.**
- **Benzene attracts _____ due to electron density in its ring.**
- **A new bond is formed as a _____ in benzene is lost.**
- **Reaction has high _____ energy and proceeds slowly.**
- **An electron pair from benzene is attracted to the _____, causing a disruption in the delocalized pi electron symmetry.**
- **Unstable carbocation _____ has both entering group and leaving hydrogen temporarily bonded.**

- **H^+ leaves, forming more stable, _____ neutral product.**



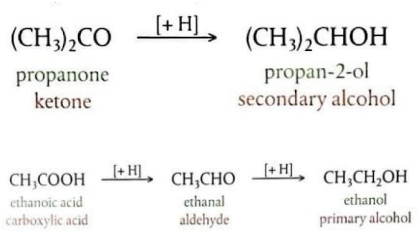
Slide 32: Electrophilic Substitution Reaction: Nitration of benzene

- **_____ of -H in benzene by $-NO_2$ to form nitrobenzene. Electrophile is NO_2^+ (nitronium ion) that is generated by mixing concentrated nitric and sulfuric acid at 50°C.**
- **Sulfuric acid _____ nitric acid to produce NO_2^+**
- **NO_2^+ is a strong _____ that forms the carbocation intermediate.**
- **H^+ is lost and binds to HSO_4^- to reform H_2SO_4**



Slide 33: Reduction Reactions

- **In organic reactions, reduction is _____ by a gain of hydrogen.**
- **_____ of Carbonyl Compounds**
- Reversal of _____ reactions can occur using a reducing agent such as:
- *sodium _____ ($NaBH_4$) in aqueous or alcoholic solution
- *lithium aluminum hydride ($LiAlH_4$) in anhydrous _____ (e.g. dry ether and aqueous acid).
- Reducing reagents produce hydride (H^-) that acts as a _____ on electron-deficient carbonyl carbon.
- Reaction of _____ acids cannot be stopped at aldehyde step due to the quick reaction.
- $LiAlH_4$
- $LiAlH_4$
- $NaBH_4$

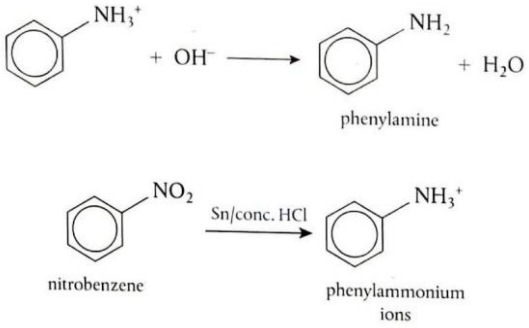


Slide 34: Reduction Reactions

- **Reduction of _____**
- _____ converted into phenylamine in 2-step reduction

process.

- $C_6H_5NO_2$ heated with Sn and concentrated HCl under reflux to produce _____ ions ($C_6H_5NH_3^+$)
- $C_6H_5NH_3^+$ is reacted with NaOH to produce _____ ($C_6H_5NH_2$)

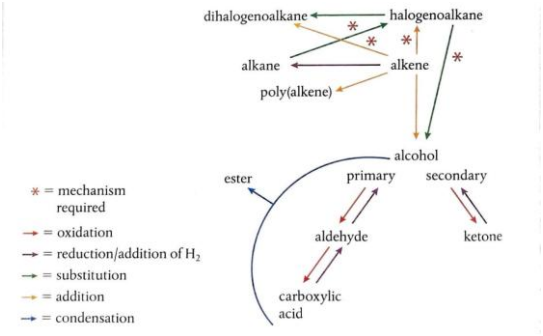


Slide 35: You Try!

- Explain how the following reduction reactions are carried out in the laboratory:
- Propanoic acid to propanol
- Nitrobenzene to phenylamine
- Ethanal to ethanol

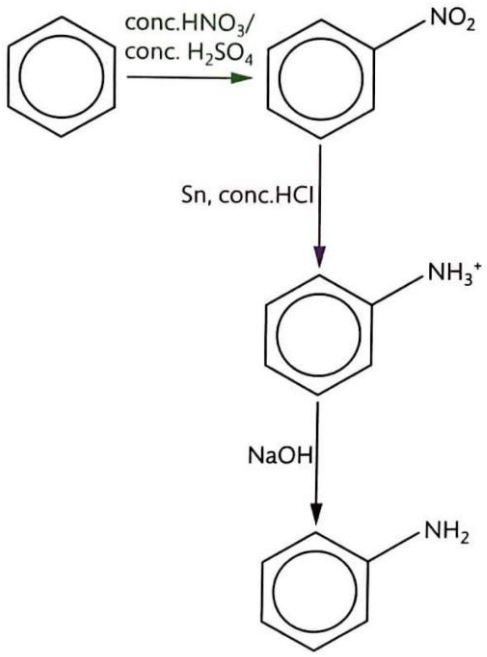
Slide 36: Organic Synthesis Routes

- Major part of drug design and industrial chemistry (e.g. dyes, clothing, _____ materials, etc.)



Slide 37: Organic Synthesis Routes

- Oil industry is main source of organic _____, but these often have to be converted from one form into another using several reactions in sequence.
- **Synthetic route:** series of steps involved in production of an organic compound that involves functional group _____



Slide 38: Retro-Synthesis

- _____ by E.J. Corey (won Nobel Prize in 1990).
- Target molecule serves as starting point, which can be converted into _____ until it becomes the starting material from which synthetic sequence can start.
- **_____ analysis:** describes the systematic backwards approach to the synthesis of organic molecules. It is now a major aspect of pharmaceutical industries.
- Fun Fact: synthetic _____ were developed from retrosynthetic analysis.

Slide 39: You Try!

- Explain how propyl propanoate can be synthesized from a single carboxylic acid. Give equations and conditions for all reactions and state type of reaction that occurs at the functional group at each step.

Slide 40: Isomerism

compounds with the same molecular formula but different arrangements of the atoms

- Structural Isomerism
- atoms and _____ groups attached in different ways

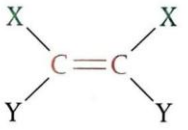
- Stereoisomerism
- different spatial _____ of atoms in molecules
- _____ Isomerism
- can be _____ only by breaking covalent bonds
- *cis-trans* and *E/Z* _____
- exist where there is _____ rotation around atoms
- _____ Isomerism
- can be _____ by free rotation about σ bonds
- Optical Isomerism
- chirality exists where there is an _____ carbon atom

Slide 41: cis-trans and E/Z isomers

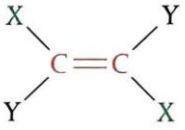
- Molecules with _____ rotation have to be described with respect to a reference plane.
- **2 cases** where they occur:
- Double-bonded _____
- Free _____ not possible because it would push p orbitals out of position, breaking the pi bond.
- The reference plane is _____ to the sigma bonds and passes through the double bond.
- Cyclic molecules
- Ring of carbon atoms _____ rotation
- Bond angles are strained from _____ angles in parent alkane
- The _____ plane is the plane of the ring

Slide 42: cis-trans isomers

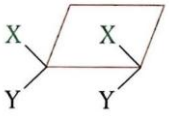
- Double-bonded _____
- Cyclic molecules
- If 2 or more _____ groups are attached to double bond or ring, they can be arranged to give 2 different isomers
- cis: groups are on **same** side of the double bond/ring
- trans: groups are on **_____** sides of the double bond/ring



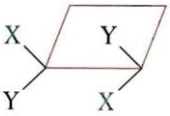
cis isomer



trans isomer



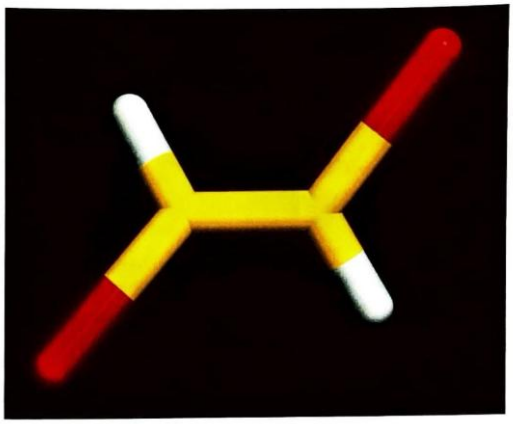
cis isomer

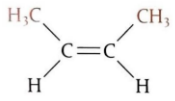


trans isomer

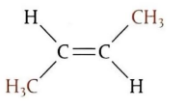
Slide 43: cis-trans isomers

- *cis*-1,2-_____
- *trans*-1,2-_____
- **Note: the _____ groups do not have to be on adjacent carbon atoms**

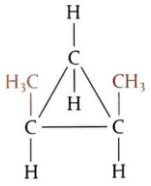




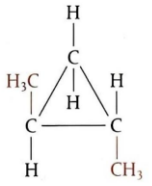
cis-but-2-ene



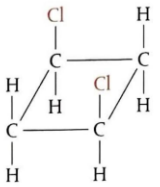
trans-but-2-ene



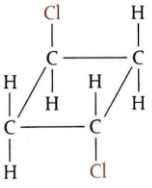
cis-1,2-dimethylcyclopropane



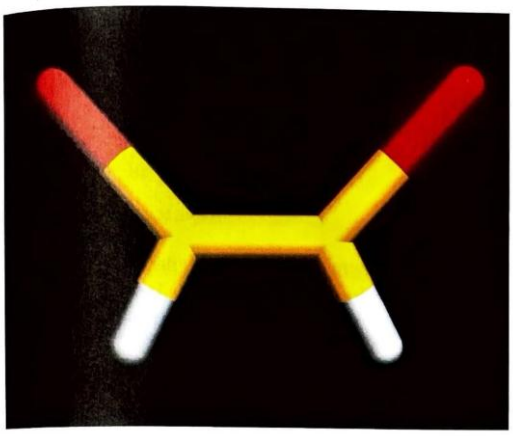
trans-1,2-dimethylcyclopropane



cis-1,3-dichlorocyclobutane



trans-1,3-dichlorocyclobutane

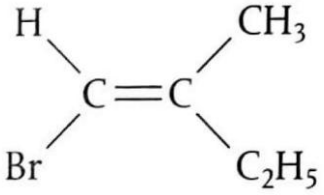


Slide 44: You Try!

- Draw and name the *cis-trans* isomers of butenedioic acid.

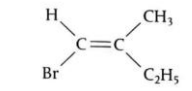
Slide 45: E/Z isomers

- Rule 1:
- The atom with the higher atomic number has _____.
- Rule 2:
- Longer _____ chains have higher priority
- Rule 3:
- Compare _____ of highest priority groups. If 2 highest priority groups are on the **same side** of the double bond, then it is *Z* isomer. If 2 highest priority group are on the **opposite side** of the double bond, then it is the *E* isomer.
- For compounds that have more than two different _____, the *E/Z* isomer naming system is used.
- **Based on the Cahn-Ingold-Prelog rules of _____**

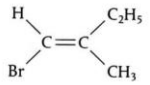


Slide 46: E/Z isomers

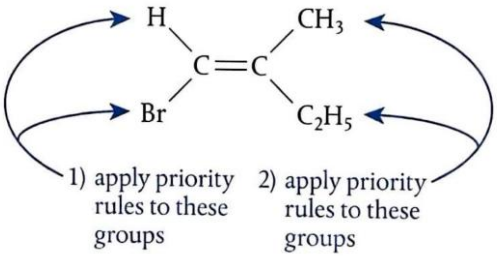
- $C_3H_7 > C_2H_5 > CH_3 > H$
- Br > Cl > F
- Physical property data (boiling point, melting points, and _____) are reported separately for each isomer.



(Z)-1-bromo-2-methylbut-1-ene



(E)-1-bromo-2-methylbut-1-ene

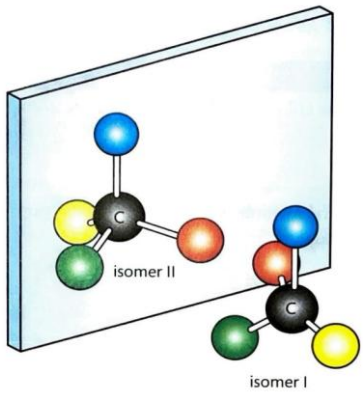


Slide 47: You Try!

- Draw and name, using the E/*Z* convention, the two stereoisomers of 3-methylpent-2-ene

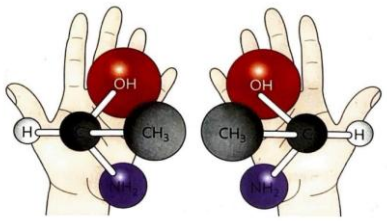
Slide 48: Optical isomers

- Refers to organic _____ with a **chiral carbon atom**
- a carbon atom attached to four different atoms/groups; aka asymmetric or a _____
- **4 groups are arranged _____ around the carbon atom (bond angles 109.5°)**
- **can be arranged in 3-D _____ that are non-superimposable mirror images of each other.**
- **are chiral _____ and have no plane of symmetry**
- form optical isomers



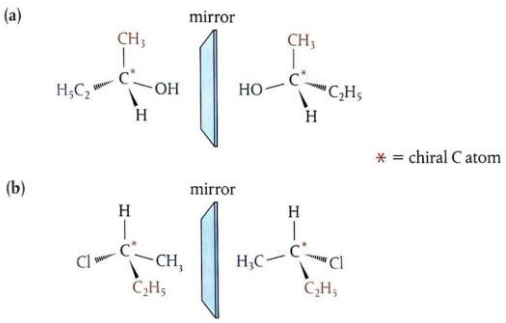
Slide 49: Enantiomers

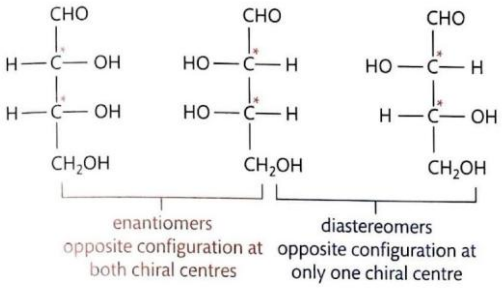
- **If a mixture contains equal amounts of the 2 _____, it is known as a racemic mixture.**
- **Molecules can have more than one chiral center, so can have multiple _____ at each one.**
- **If molecules have different optical _____ at one or more, but not all, chiral centers, they are diastereomers.**
- not mirror images of each other
- non-_____ optical isomers



Slide 50: Enantiomers

- sugars are often _____ of each other
- chiral centers are often marked with an _____
- Fun fact: nearly all amino acids are chiral, but usually only one form occurs in _____ systems.

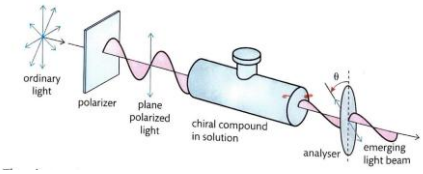




Slide 51: You Try!

- Draw the enantiomers of 2-hydroxypropanoic acid (lactic acid). Mark the chiral carbon atom and show the plane of the mirror.

Slide 52: Properties of Enantiomers



- _____ have identical physical and chemical properties, with 2 exceptions
- Optical Activity
- have different _____ with light
- if a beam of plane-polarized light (light waves oscillating in a single plane) is passed through a solution of optical isomers, they rotate the plane of _____.
- A racemic mixture of _____ rotate light in equal but opposite directions, so are **optically inactive.**
- Chiral molecules that exist as only one enantiomer are **optically active**. If an enantiomer rotates light clockwise, it is designated (+, sometimes “d”). If it rotates light _____, it is designated (-, sometimes “l”).

Slide 53: Properties of Enantiomers

- _____ with other chiral molecules
- If a **racemic mixture** is reacted with a single enantiomer of a different compound, the two original _____ react to produce different products with distinct chemical and physical properties.
- this is known as resolution and is a way to separate _____ from a racemic mixture
- A not-so-fun fact:
- Biological systems are chiral environments, so react differently with enantiomer pairs. Thalidomide was a drug prescribed for morning sickness in the 1960s. One enantiomer is therapeutic, while the other produces

_____ in the fetus. This sad tragedy did lead to the process of asymmetric synthesis, in which a single enantiomer is produced using a chiral catalyst.

Slide 54: 4.5: Spectroscopic identification of organic compounds

Slide 55: How do scientists identify unknown substances?

- Chemical analysts identify and characterize unknown substances to determine the composition of a mixture and identify impurities.
- **Qualitative analysis** – **detects the presence but not amount of a substance in a mixture**
- **Quantitative analysis** – **measures the quantity of a substance in a mixture**
- **Structural analysis** – **describe how atoms are arranged in a molecular structure**

Slide 56: Instrumentation

- **Infrared _____:** used to identify bonds in molecules
- **Mass spectrometry:** used to determine relative atomic and molecular masses using the _____ pattern of the molecules
- **Nuclear magnetic resonance _____ (NMR):** uses isotopes to give structural information
- **A _____ of techniques can give evidence of molecular structure.**

Slide 57: Mass Spectrometry

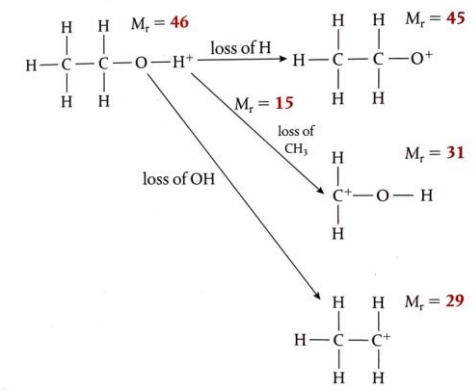
- **Mass _____ is primarily used to determine the molar mass and formula for a compound**
- A compound is _____ and then ionized
- The masses of the ions are _____ and graphed

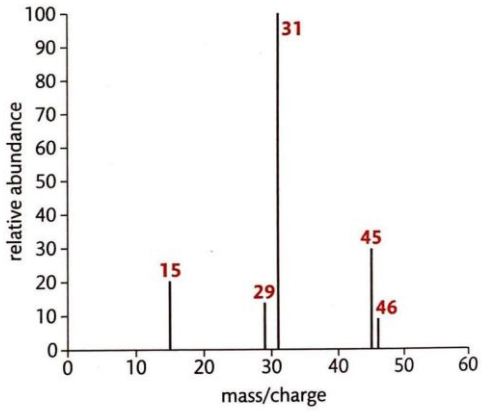
Slide 58: Fragmentation Patterns

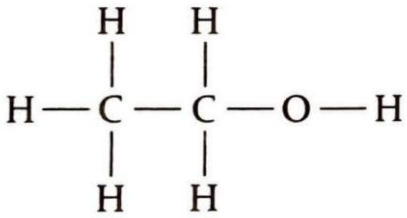
- The _____ process in the mass spec involves **removing an electron** to produce a **positive ion** by a **collision**.
- The _____ can be so energetic that it causes the molecule to **split into different fragments**.
- The **largest mass peak** _____ to the **parent ion (**the molecule that has **lost one electron)** passing through unscathed.
- The parent ion can then break into other smaller ions, or _____ that are detected.
- The mass spec _____ pattern can provide useful evidence for the structure of a compound.

Slide 59: Analyzing fragmentation patterns

- **Possible fragmentation pattern of ethanol**
- **Parent ion**
- **Why do you think the peak at 31 is the most abundant?**







Slide 60: Fragmentation Patterns

- You are expected to _____ the following mass

fragments (Data booklet table 28)

Mass lost	Fragment lost
15	$CH_3\cdot$
17	$OH\cdot$
18	H_2O
28	$CH_2{=}CH_2$, $C{=}O\cdot$
29	$CH_3CH_2\cdot$, $CHO\cdot$
31	$CH_3O\cdot$
45	$COOH\cdot$

Slide 61: Remember, MS only detects charged fragments

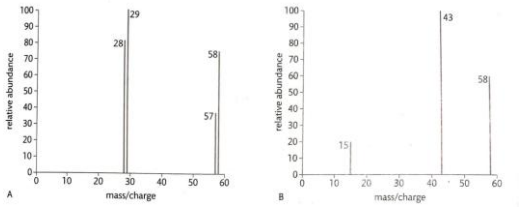
- **_____ THE FRAGMENTS-Pentane**
- **M-29**
- **M-15**
- **M-43**
- **M-57**

Slide 62: Groupings of peaks are due to the presence of molecular isotopes.

- **_____ THE FRAGMENTS-Pentane**
- **M-57**
- **M-43**
- **M-29**
- **M-15**
- **M-72**

Slide 63: You Try!

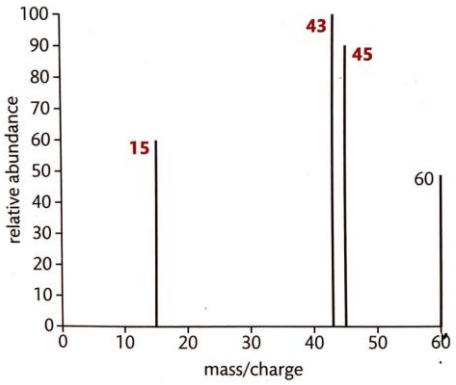
- Two mass spectra are shown . One is propanone and other is propanal. Identify the spectra that belongs to each compound, explaining the similarities and differences in each.



Slide 64: You Try!

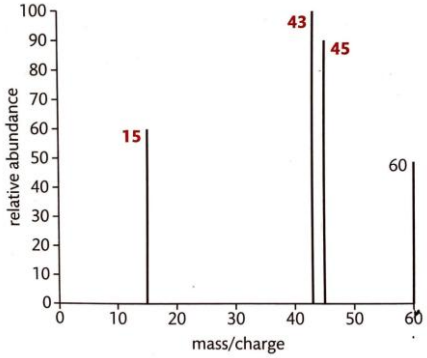
Slide 65: Determining molecular formula from mass spectrum

- _____ **Formula**: CH_2O
- _____ **Formula**: $C_nH_{2n}O_n$
- $M_r = n(12.01)+2n(1.01)+n(16.00) = 30.03n$
- $M_r = 60$
- $60 = 30.03n$
- $n = 60/30.03 = 2$
- _____ Formula: $C_2H_4O_2$



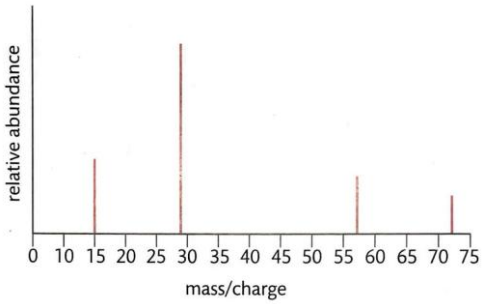
Slide 66: Determining molecular structure from mass spectrum

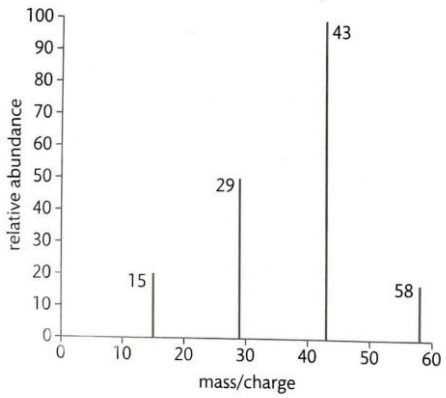
- **Step 1:** Identify formula of peak _____
- **60:** $C_2H_4O_2$ (parent _____)
- **45:** $COOH^+$
- _____ from 60-15 (loss of CH_3 from parent)
- **43:** Not _____ from IB booklet, but
- _____ from 60-17 (loss of OH from parent)
- Indicates fragment _____ $C_2H_3O^+$
- **15:** CH_3^+
- _____ from loss of COOH from parent
- **Step 2:** Identify _____ of smaller peak fragments
- **Step 3:** Combine _____ structures to determine parent structure



Slide 67: Let's Practice!

- The formula of a compound is $C_nH_{2n}O$. What ions are observed in the mass spectrometer?
- The empirical formula of a compound is C_2H_5. What ions give rise to the peaks below? Deduce the molecular structure of the compound.





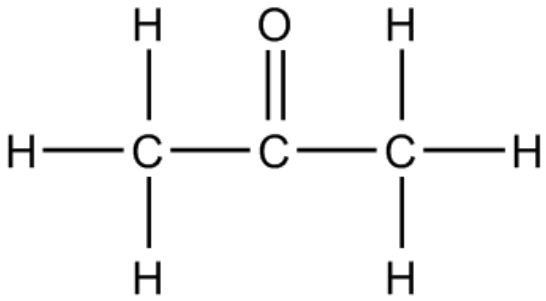
Slide 68: Degree of unsaturation

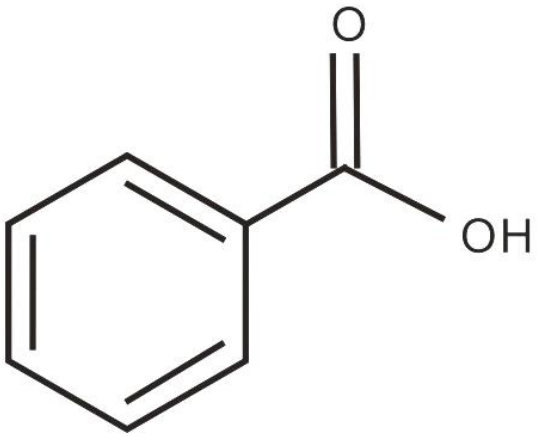
- The degree of _____ is also known as the **index of hydrogen deficiency (IHD)**
- **a measure of how many molecules of H_2 that are needed to convert the molecule to a _____ saturated, non-cyclic molecule.**
- This provides a useful clue to the _____ of a molecule once its formula is known.

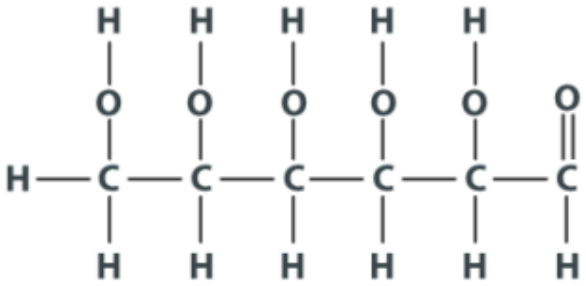
Slide 69: IHD Values

Molecule	Saturated non-cyclic target	Index of hydrogen deficiency (IHD)
C_2H_4	C_2H_6	1
C_2H_2	C_2H_6	2
cyclobutane and but-1-ene, C_4H_8	C_4H_{10}	1
C_2H_5OH	C_2H_5OH	0
C_2H_4O	C_2H_6O	1
C_2H_5Cl	C_2H_5Cl	0

Slide 70: Determining IHD Values





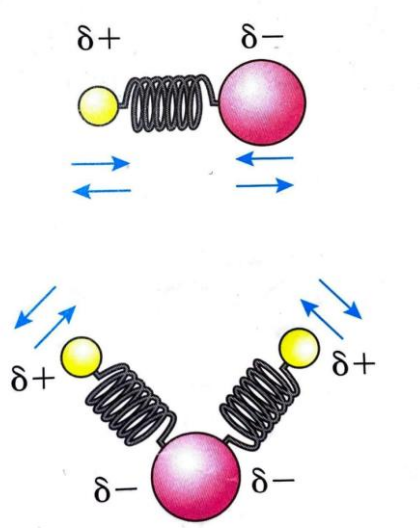


Slide 71: Electromagnetic Spectrum and Molecular Structure

- Spectroscopy involves an interaction between matter and light (_____ radiation)
- Light can be thought of as waves of energy or packets (_____) of energy called photons
- _____ of light waves include wavelength ($\boldsymbol{\lambda}$) and frequency ($\boldsymbol{\nu}$)
- **Distance between _____ wave crests**
- **Number of waves which pass a point every second**

Slide 72: Infrared (IR) Spectroscopy

- A _____ bond can be thought of as a spring.
- Each bond in a molecule **vibrates** and **bends** at a **natural** _____ depending on the **bond strength** and **masses** of atoms.
- **Light** atoms vibrate at **higher** _____ than heavier atoms.
- **Multiple bonds** vibrate at **higher** _____ than single bonds.
- Bonds can be identified based on the _____ at which they absorb energy.
- **Stretching**
- **Bending**
- **# of waves per _____**

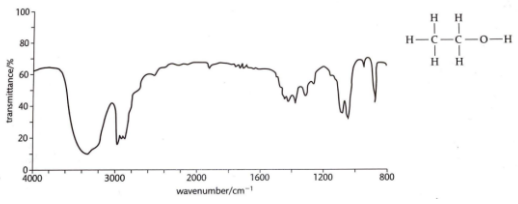


Slide 73: IR Spectroscopy

- Simple diatomic _____ (e.g. HCl, HBr and HI) can only vibrate when the bond stretches.
- **HCl** bond has the **highest _____** because Cl is the lightest of these three halogens.
- _____ types of vibration (i.e. **bending**) occur in more **complex** molecules.
- The energy needed to excite the bonds in _____ and make them vibrate with greater amplitude occurs in the **IR region**.
- Only **polar _____** will **interact with IR radiation** (**nonpolar** molecules **cannot interact** with an electric field).
- Polar molecules have partial positive and negative charges that change due to change in _____ energy when IR radiation is absorbed.
- **Polarity = IR _____**
- **Change in dipole moment = "IR active"**

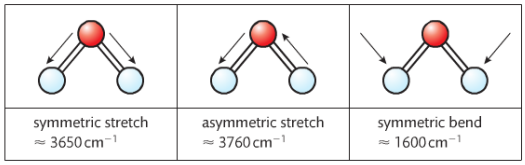
Slide 74: IR Example-Ethanol

- ***Notice how the x-axis is nonlinear**
- ***100% transmittance = no IR absorption**
- **Different "bands" represent different chemical bonds**

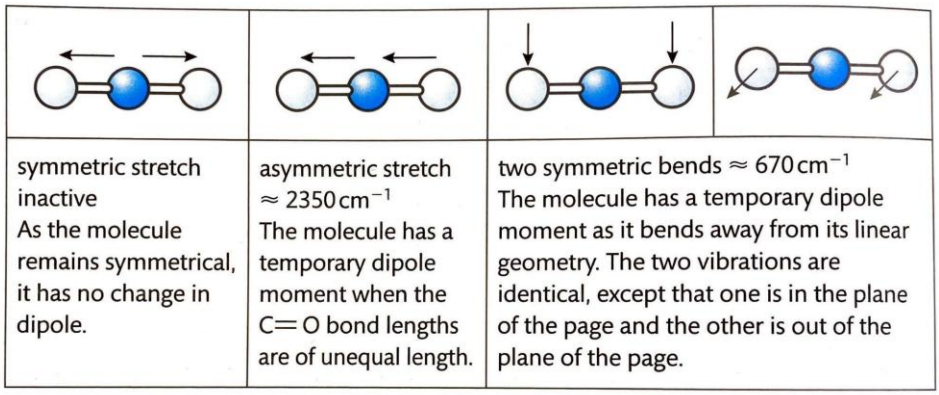


Slide 75: Polyatomic Molecules

- It is more correct to consider the _____ molecule stretching and bending as a whole, rather than individual bonds.
- Water has **three _____ modes** detected by IR radiation:
- Symmetric stretch
- Asymmetric stretch
- Symmetric bend
- These are all IR active in water!



Slide 76: CO_2 Vibration Modes



symmetric stretch inactive As the molecule remains symmetrical, it has no change in dipole.	asymmetric stretch ≈ 2350 cm^{-1} The molecule has a temporary dipole moment when the C═O bond lengths are of unequal length.	two symmetric bends ≈ 670 cm^{-1} The molecule has a temporary dipole moment as it bends away from its linear geometry. The two vibrations are identical, except that one is in the plane of the page and the other is out of the plane of the page.

Slide 77: IR absorption bands

- Position of IR absorption depends on bond environment
- ***Why do you think some of the C-C bonds produce an IR absorption band?**
- **Found on Table 26 of the Data Booklet**
- **Hydrogen bonds broaden absorption bands and shift to lower frequency**

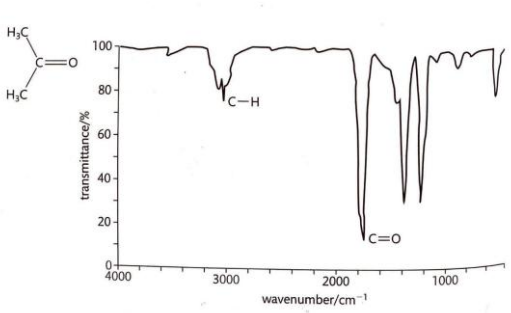
Slide 78: IR Absorption Range

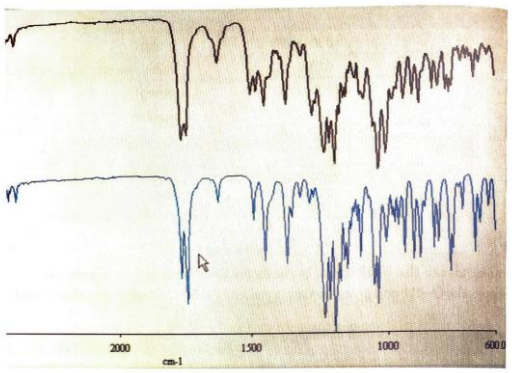
- The absorption of particular _____ of IR radiation helps the chemist identify the bonds in a molecule.

Slide 79: IR Absorption Range

Slide 80: IR Peak Shapes

- Some bonds can be identified by the distinctive shape of their signals:
- OH gives a broad signal
- C=O gives a sharp signal
- **propanone**
- IR spectroscopy can be used to identify compounds in unknown samples.
- **Known Standard**
- **Unknown sample**
- ***What would you conclude about the unknown sample from the IR spectra?**





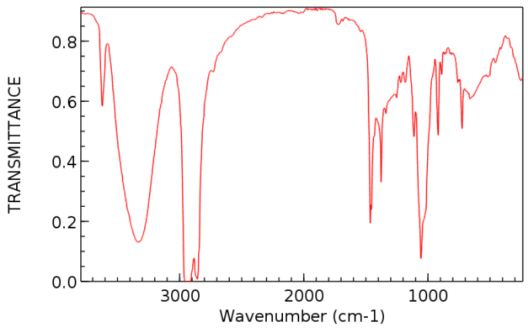
Slide 81: The Fingerprint Region

- Although the entire IR spectrum can be used as a _____ for the purposes of comparing molecules, the **600 - 1400 cm^{-1}** range is called the **fingerprint region**. This is normally a complex area showing many bands, frequently overlapping each other. This complexity limits its use to that of a fingerprint, and should be ignored by beginners

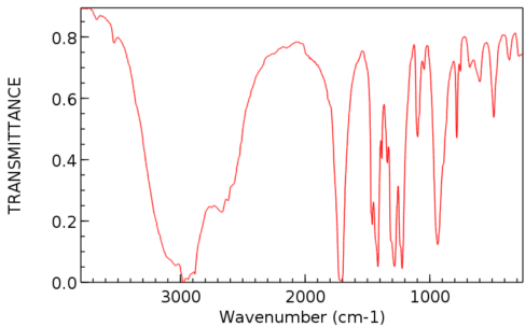
when analyzing the spectrum. As a student, you should focus your analysis on the rest of the spectrum, that is the region to the left of 1400 cm^{-1}

Slide 83: Let's Practice!

- Options: Butanoic acid, hexanal, 1-hexanol, 1-hexene



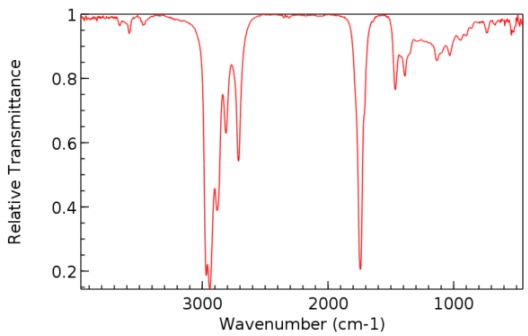
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)



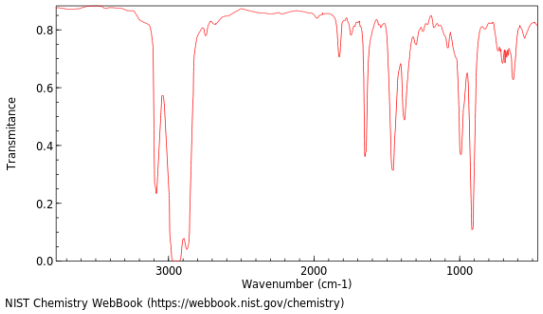
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Slide 84: Let's Practice!

- Options: Butanoic acid, hexanal, 1-hexanol, 1-hexene



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

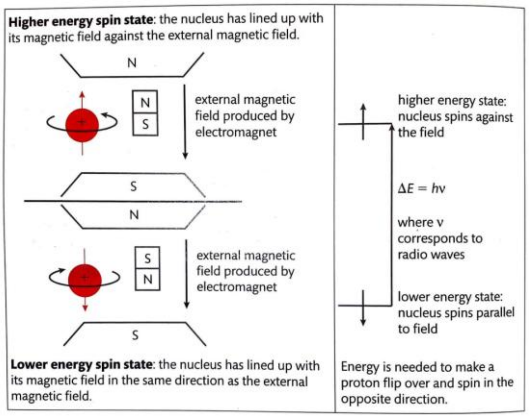


Slide 85: Nuclear Magnetic Resonance Spectroscopy (NMR)

- NMR is used to show the chemical _____ of certain isotopes (hydrogen, carbon, phosphorus and fluorine) in a molecule.
- This is a powerful _____ for finding the structure and shape of molecules.
- The nuclei of atoms with an odd number of _____ such as ^{1}H, ^{13}C, ^{19}F, and ^{31}P spin and behave like tiny bar magnets.

Slide 86: NMR Energy Levels

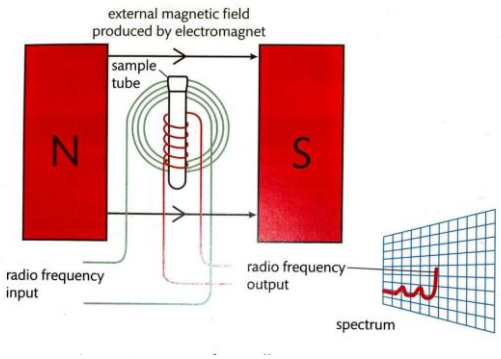
- If placed in an _____ magnetic field, some of the nuclei will line up with an applied field and some will line up against it (2 nuclear energy levels).
- Radio waves can provide the energy needed for the nuclei to reverse their spin and change their _____ in the magnetic field.



Slide 87: NMR Diagram

- An NMR sample is placed in an _____.
- The field strength is varied until the radio waves have the exact _____ needed to make the **nuclei flip over and spin in the opposite direction**.

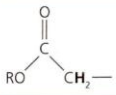
- Resonance and can be detected _____ and recorded in the form of a spectrum.
- **Resonance**

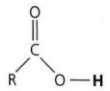
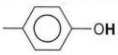
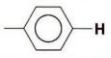


Slide 88: ^{1}H-NMR Spectroscopy

- _____ shield nuclei from full effects of external magnetic field
- Different electron _____ produce different energy separations between spin levels
- This means nuclei in different chemical _____ produce different signals in NMR spectrum
- Signals give _____ about atomic position in molecules
- Sample peaks are compared to a standard (_____) to indicate the number and environment of proton atoms.
- **_____ shift: position of NMR signals relative to a standard**
- **_____ (TMS)**

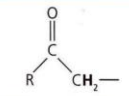
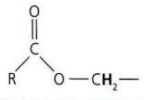
Slide 89: ^{1}H-NMR Spectroscopy-Chemical Shifts

Type of proton	Chemical shift / ppm
TMS	0
$-CH_3$	0.9–1.0
	2.0–2.5

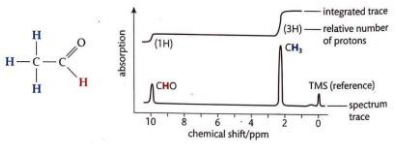
	9.0–13.0*
R—O—H	1.0–6.0*
—HC=CH_2	4.5–6.0
	4.0–12.0*
	6.9–9.0
	9.4–10.0

* Signals from the hydrogen atoms in the —OH groups are very variable owing to hydrogen bonding.

Type of proton	Chemical shift / ppm

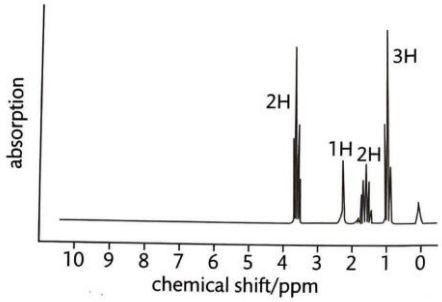
	2.2–2.7
—C≡C—H	1.8–3.1
R—O—CH_2—	3.3–3.7
	3.7–4.8

Slide 90: ^{1}H-NMR Spectroscopy



- **_____ obtained from a ^{1}H NMR spectrum:**
- the **number of resonance signals** denotes the number of different (non-_____) hydrogen atoms present
- **_____ of the peak areas** gives the relative number of hydrogens causing the resonance
- the **chemical shift** reveals the electronic bonding _____ of the hydrogens
- **"Steps" are _____ to the # of protons**

Slide 91: Analyzing a ^{1}H-NMR Spectrum: C_3H_8O



- **TMS standard peak**
- —C**H**$_3$
- —C**H**$_2$R
- R–O–**H**
- R–O–C**H**$_2$–
- **_____ structure of compound:**

Slide 92: Let's Practice!

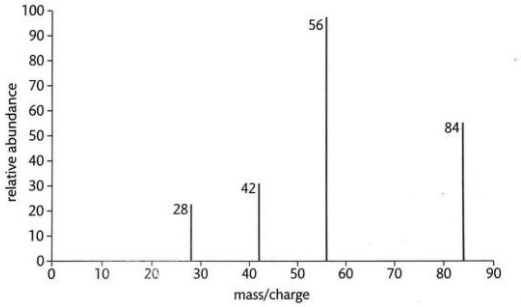
- **State the purpose of the TMS peak.**
- **What are the functional groups responsible for the signals at each location on the spectrum?**
- **Identify the unknown compound and draw its structure.**

Slide 93: Combining analytical techniques

- **A _____ of analytical methods is often used to provide the most complete structure of compounds being studied.**
- **1. Deduce the _____ formula of the compound.**
- **2. From the mass spectrum, deduce the _____ formula and IHD of the compound.**

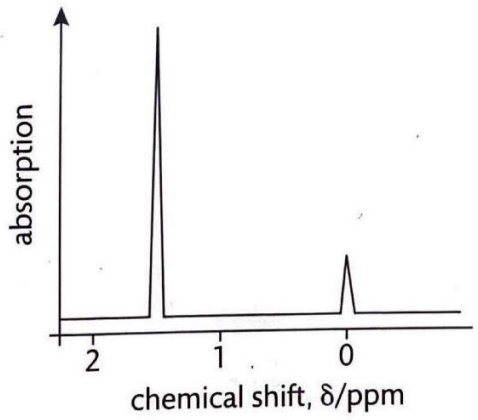
(a) An unknown compound is found to have the following composition

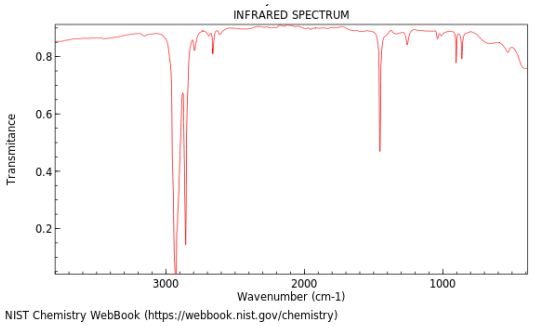
	% composition by mass
C	85.6
H	14.4



Slide 94: Combining analytical techniques

- **3. Deduce the _____ structure from the IR and ^{1}H NMR spectrum.**





NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

Slide 95: Tetramethylsilane (TMS) Reference

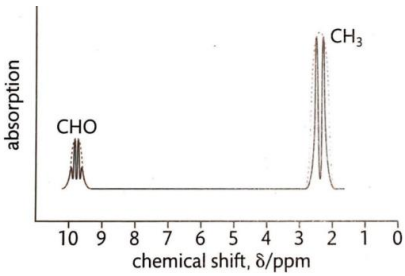
- One signal is recorded in TMS due to all hydrogens being in the same chemical _____.
- TMS standard does not overlap with other signals in a spectra because TMS absorbs radio waves in a _____ region
- Si has a lower _____ than C
- _____ shift (δ) of proton in a molecule:
- $\boldsymbol{v}$-$\boldsymbol{v}_0$
- $\boldsymbol{v}_0$
- **δ** =
- { }
- × 10^6 ppm
- $\boldsymbol{v}$: _____ of radio waves absorbed by the protons in the sample
- $\boldsymbol{v}_0$: _____ of radio waves absorbed by the protons in TMS
- **The _____ shift relative to the standard stays the same!**

Slide 96: Benefits of TMS

- **Chemically inert**
- **Soluble in most organic _____**
- **Low boiling point**
- **Easily _____ from most samples**

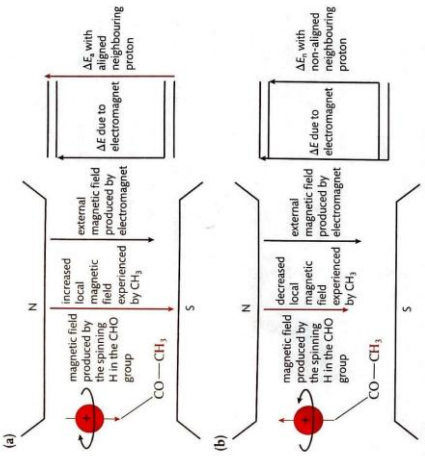
Slide 97: High-resolution ^{1}H NMR spectroscopy

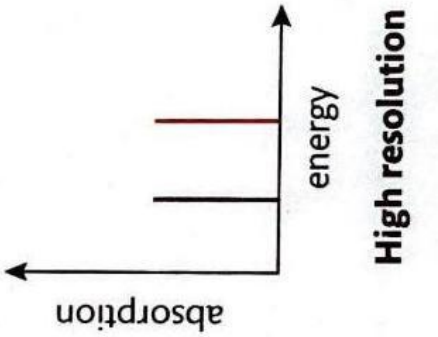
- Low-_____ NMR usually shows single peaks
- High-_____ NMR shows split peaks
- Occurs due to **spin-spin _____**
- Local magnetic field is increased when _____ proton magnetic field is aligned with external magnetic field and decreased when aligned against it.
- **Ethanal**
- **nuclei magnetic fields being modified by magnetic fields of _____ protons**
- **Two signals produced from the CHO proton _____ with the CH_3 protons**
- **Four signals produced from the CH_3 protons _____ with the CHO proton**

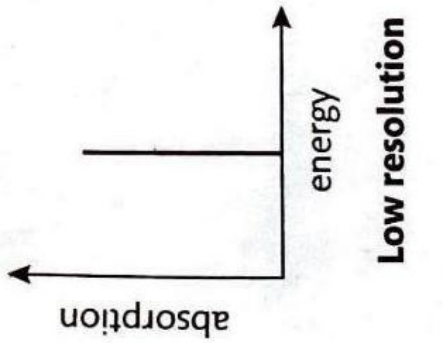


Slide 98: Splitting of energy levels

- **ΔE**: energy _____ between the spin states of a proton
- **ΔE_a**: alignment of magnetic field with _____ proton
- **ΔE_n**: non-alignment of magnetic field with _____ proton
- **One signal in a low-resolution spectrum produces a doublet in a high-resolution spectrum due to the influence of the proton on a _____ carbon atom.**

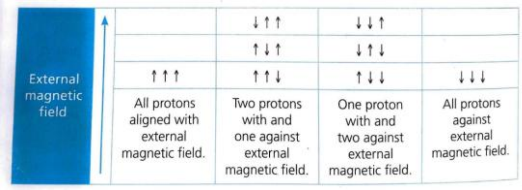


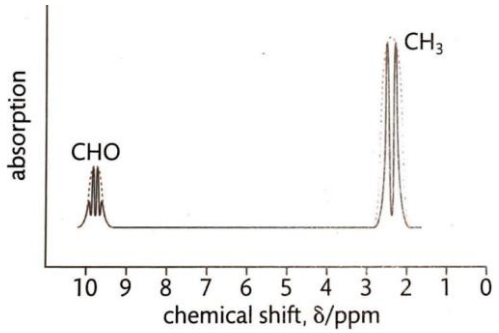




Slide 99: Splitting due to -CH_3 protons

- **Neighboring -CH_3 protons have different spin _____, producing magnetic fields that split the NMR peak.**
- **Relative _____ of peaks: 1, 3, 3, 1**





Slide 100: Splitting due to -CH_2 protons

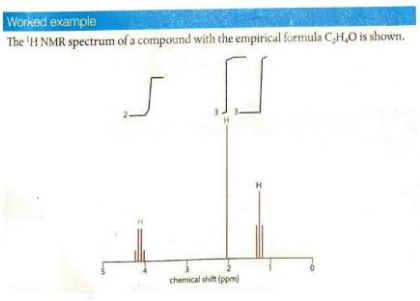
- **Three lines are produced with relative _____ of 1, 2, 1**

Slide 101: ^{1}H-NMR Summary

- **Protons bonded to the same atom do not _____ with each other (behave as a group)**
- **Protons on non-adjacent carbon atoms _____ do not interact with each other**
- **The O-H single peak in ethanol doesn't split unless the sample is pure (rapid exchange of protons between ethanol _____ averages out spins).**
- **For for a proton with *n* protons as its nearest _____(s), its NMR peak is split into (*n* + 1) peaks.**

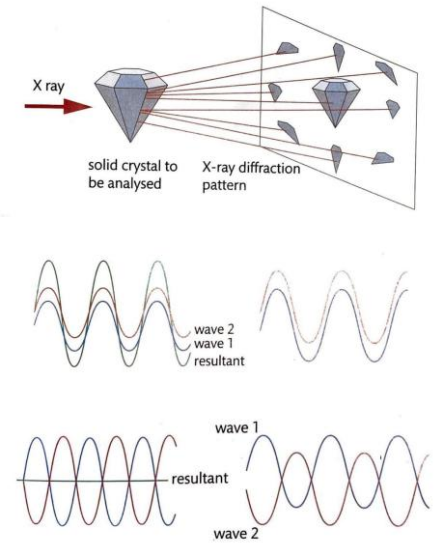
Slide 102: Let's Practice!

- **Deduce the molecular formula of the compound.**
- **Draw possible structures of molecules with this molecular formula.**
- **Use section 27 of the Data Booklet to identify a structure which is consistent with the ^{1}H NMR spectrum, account for the number of peaks, and the splitting patterns in the spectrum.**
- ***Note: chemical shifts may not exactly match the Data Booklet values.**



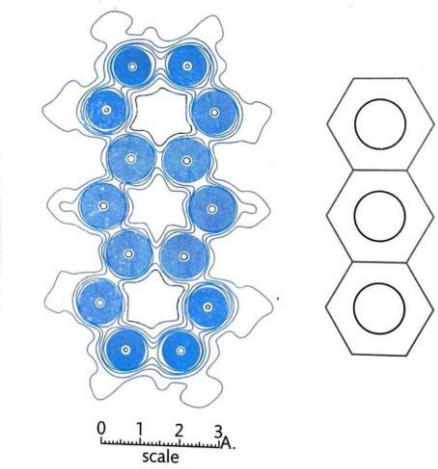
Slide 103: X-Ray Diffraction

- Passing X-rays(10^{-9} m) through a _____ solid interact with electrons in the substance and are scattered in an orderly way.
- Scattered waves interfere with each other to cause a _____ **pattern**.
- Interaction of waves can cause _____ **interference** or **destructive interference**.
- **Waves are in phase, _____ each other**
- **Waves are out of phase, cancel each other out.**



Slide 104: DIFFRACTION PATTERN

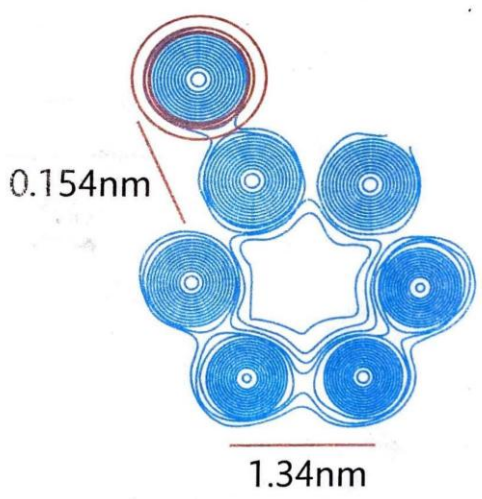
- Sample must be in the solid state (only solids give ordered _____ patterns).
- Scattered waves are at different phases depending on their _____ when they hit the detector.
- Diffraction pattern is dependent on the _____ between angle of incidence (θ), wavelength of incident X-rays (λ), and the distance between and relative orientations of atoms (***d***).
- Electron density map can be determined from the _____ pattern.
- Atom identities can be determined from electron density map (related to electron _____).
- _____ atoms not visible (e^- density too low).
- Used to identify _____ molecular structures (organic and inorganic).
- Bond lengths and angles can be _____ from the e^- density map.
- **High e^- density between atoms _____ covalent bonds.**
- **e^- density map of _____**
- **_____ lines connect points with same e^- density.**



Slide 105: Let's Practice!

- Identify the compound from its bond length data.
- Explain why not all the atoms are shown in the electron density map.

- Deduce the degree of IHD of the compound.
- 0.134 nm
- 0.154 nm



Slide 106: Table of Contents

- 21.1: Although spectroscopic _____ techniques form the backbone of structural identification of compounds, typically no one technique results in a full structural identification of a molecule.
- **Essential Ideas**

Slide 107: 21.1 Understandings

- Structural _____ of compounds involves several different analytical techniques, including IR, ^{1}H NMR, and MS.
- In a high-_____ ^{1}H NMR spectrum, single peaks present in low resolution can split into further clusters of peaks.
- The structural technique of single X-ray _____ can be used to identify the bond lengths and bond angles of crystalline compounds.

Slide 108: 21.1 Applications and skills

- Explanation of the use of _____ (TMS) as the reference standard.
- Deduction of the structure of a compound given information from a range of analytical _____ techniques (X-ray crystallography, IR, ^{1}H NMR, and MS.

Slide 109: Tetramethylsilane (TMS) Reference

- One signal is recorded in TMS due to all hydrogens being in

the same chemical _____.

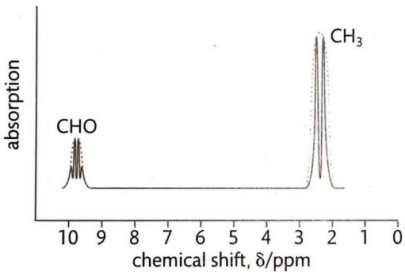
- TMS standard does not overlap with other signals in a spectra because TMS absorbs radio waves in a _____ region
- Si has a lower _____ than C
- _____ shift (δ) of proton in a molecule:
- $\boldsymbol{v}$-$\boldsymbol{v}_0$
- $\boldsymbol{v}_0$
- **δ** =
- [ ]
- ✕ 10^6 ppm
- $\boldsymbol{v}$: _____ of radio waves absorbed by the protons in the sample
- $\boldsymbol{v}_0$: _____ of radio waves absorbed by the protons in TMS
- **The _____ shift relative to the standard stays the same!**

Slide 110: Benefits of TMS

- **Chemically inert**
- **Soluble in most organic _____**
- **Low boiling point**
- **Easily _____ from most samples**

Slide 111: High-resolution ^{1}H NMR spectroscopy

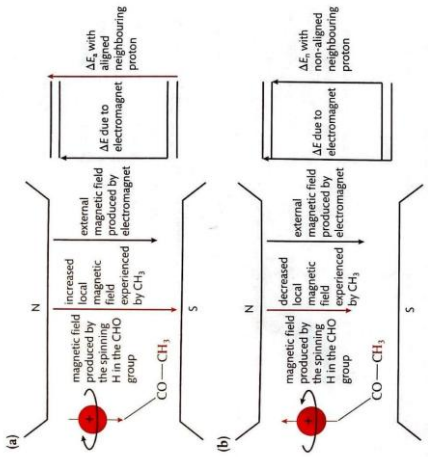
- Low-_____ NMR usually shows single peaks
- High-_____ NMR shows split peaks
- Occurs due to **spin-spin _____**
- Local magnetic field is increased when _____ proton magnetic field is aligned with external magnetic field and decreased when aligned against it.
- **Ethanal**
- **nuclei magnetic fields being modified by magnetic fields of _____ protons**
- **Two signals produced from the CHO proton _____ with the CH_3 protons**
- **Four signals produced from the CH_3 protons _____ with the CHO proton**

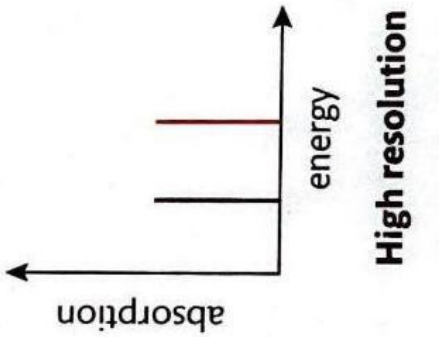


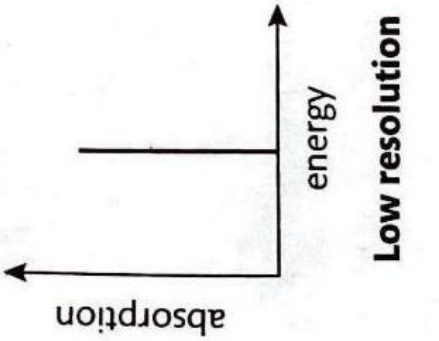
Slide 112: Splitting of energy levels

- **Δ*E***: energy _____ between the spin states of a proton
- **Δ*E*$_a$**: alignment of magnetic field with _____ proton

- **ΔE_n**: non-alignment of magnetic field with _____ proton
- **One signal in a low-resolution spectrum produces a doublet in a high-resolution spectrum due to the influence of the proton on a _____ carbon atom.**



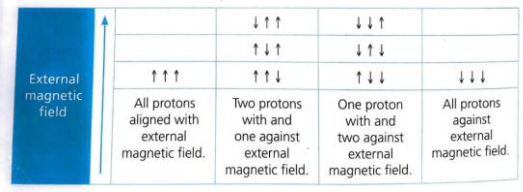


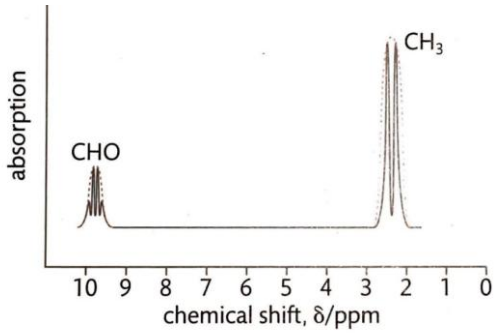


Slide 113: Splitting due to -CH_3 protons

- **Neighboring -CH_3 protons have different spin _____, producing magnetic fields that split the NMR peak.**

- **Relative _____ of peaks: 1, 3, 3, 1**





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- **Protons bonded to the same atom do not _____ with each other (behave as a group)**
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Slide 116: Let's Practice!

- **Deduce the molecular formula of the compound.**
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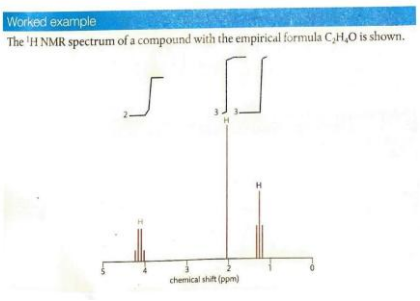

Slide 117: X-Ray Diffraction

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- Scattered waves interfere with each other to cause a _____ **pattern**.
- Interaction of waves can cause _____ **interference** or **destructive interference**.
- **Waves are in phase, _____ each other**
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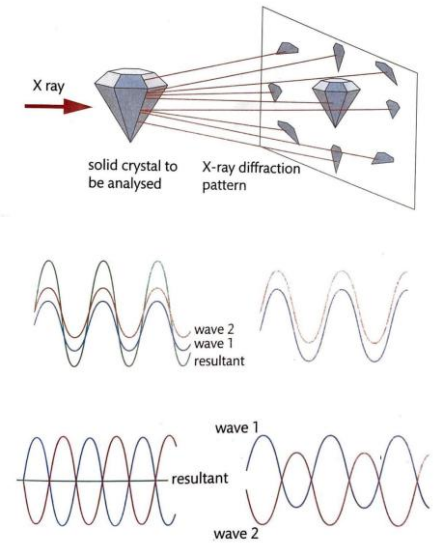

Slide 118: DIFFRACTION PATTERN

- Sample must be in the solid state (only solids give ordered _____ patterns).
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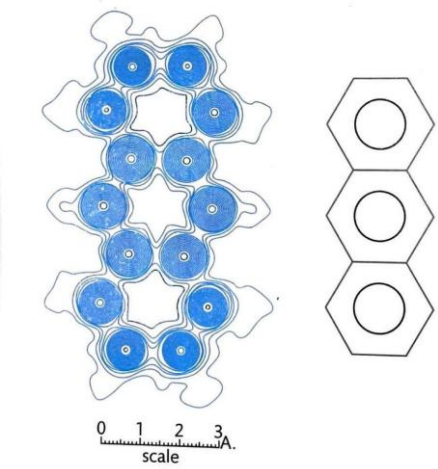
- **e^- density map of _____**
- **_____ lines connect points with same e^- density.**



Slide 119: Let's Practice!

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- Deduce the degree of IHD of the compound.
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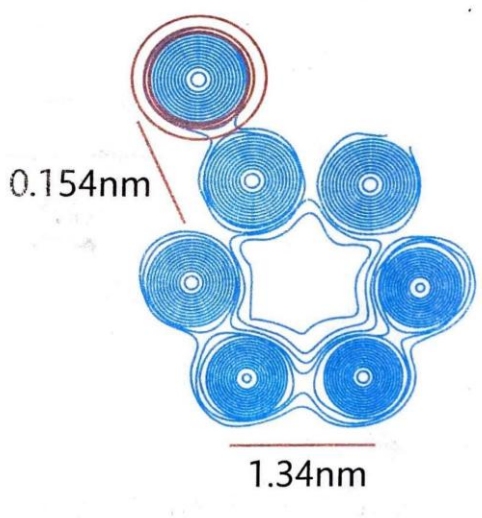

Slide 120: Citations

- _____ Baccalaureate Organization. Chemistry Guide, First assessment 2016. Updated 2015.
- Brown, Catrin, and Mike Ford. *Higher Level Chemistry*. 2nd ed. N.p.: Pearson _____, 2014. Print. ISBN 978 1 447 95975 5
- eBook 978 1 447 95976 2
- Most of the _____ found in this power point comes directly from this textbook.
- The power point has been made to directly complement the Higher Level Chemistry textbook by Brown and Ford and is used for direct _____ purposes only.