

# e-Znotes<sup>TM</sup>

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CHM 201 A2 Test 3 Fall 2000 (Dr. Snyder)

## Spectroscopy

### Mass Spec.

Mass spec *MS* is used to detect Molecular Weight *MW*. For example:



can easily be distinguished because they have different *MW*s.

### Infrared Spec.

Infrared *IR* is used to detect functional groups. For example, IR can tell the different between:

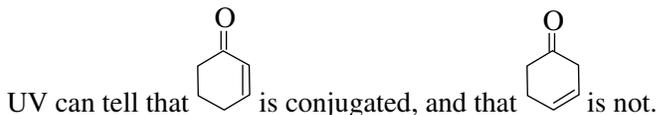


because the ether (on the left) and the alcohol absorb IR radiation at different places on the IR spectrum.

### Ultraviolet Spec.

Ultraviolet spec *UV* is used to determine if conjugation is present.

► On the back tests, conjugation is always represented as a double bond, followed by a single bond, followed by a double bond.



### Proton NMR

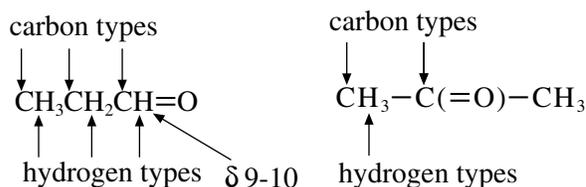
Proton NMR *H-NMR* can tell how many different types of hydrogen's are present in a compound.

For example, H-NMR can tell that acetone  $\text{CH}_3\text{-C(=O)-CH}_3$  has one type of hydrogen, and that 2-chloropropane  $\text{CH}_3\text{-CHCl-CH}_3$ , has two.

### Carbon 13 NMR

Carbon NMR  $^{13}\text{C-NMR}$  can tell how many types of carbon environments are present in a molecule. For example,  $^{13}\text{C-NMR}$  can distinguish between acetone  $\text{CH}_3\text{-C(=O)-CH}_3$  which has two types of carbon, and propanal,  $\text{CH}_3\text{CH}_2\text{CH=O}$  which has three.

■ Note: H-NMR may also be used to distinguish between the above compounds since acetone has one hydrogen type, and propanone has three (with the aldehydic H at  $\delta$  9-10).



## Trivial Pursuit

### MS Trivial Pursuit

- ▶ Neopentane and Isobutane are most likely to give a **base (tallest, most stable) peak of m/z of 57** because they form the 3° **tertbutyl carbocation**  $\text{C}^+$ .
- ▶ A peak that is **15 m/z units less** another peak (a.k.a. parent peak) indicates the presents of a **methyl group**.
- ▶ A peak that is **one, two or three m/z above the molecular ion** peak is due to **isotopes**.
- ▶ **Propene gives a base peak of 41**, which is due to the allyl  $\text{C}^+$ ,  $\text{CH}_3=\text{CH}-\text{CH}_2^+$ .
- ▶  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2=\text{CH}_2$ , would form a very stable  $\text{C}^+$  in MS – the allyl  $\text{C}^+$  (see above).
- ▶ MS is good for telling the difference between cycloheptane and cyclooctane or between cyclohexanone and cycloheptanone (MW).
- ▶ MS is best to tell the difference between  $\text{CH}_3-\text{CHBr}-\text{CHBr}$  and  $\text{CH}_3-\text{CHBr}-\text{CHCl}$  (MW).
- ▶ When  $\text{C}^+$ 's (**charged particles**) **follow a curved path in a magnetic field** and are separated based on theirs MX, that's **MS**.
- ▶ When a compound is turned into a  $\text{C}^+$  and fragments, that's **MS**.

### IR Trivial Pursuit

- ▶ An absorption at **1700  $\text{cm}^{-1}$**  indicates a carbonyl group  **$\text{C}=\text{O}$** .
- ▶ An absorption near 3200 – 3600  $\text{cm}^{-1}$  (**about 3400  $\text{cm}^{-1}$** ) indicates a **hydroxyl group  $\text{C}-\text{OH}$** .
- ▶ An absorption near **3000  $\text{cm}^{-1}$**  indicates a  **$\text{C}-\text{H}$  stretch**.
- ▶ **IR absorptions** occur with an increase in **vibrational energy**.
- ▶ IR is a great way to tell the different between  $\text{CH}_3-\text{C}(=\text{O})-\text{CH}_3$  and  $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH}$ , cause these compounds have **different functional groups**.
- ▶ Stretching of covalent bonds occurs above 1000 $\text{cm}^{-1}$  and bending occurs below.
- ▶ MS destroys the original sample.
- ▶ To identify a compound by the “fingerprint” method, a sample of the actual compound, its structure, and its spectrum would be required.
- ▶ **As opposed to a fingerprint analysis, a rational analyses** of the significant absorptions may be conducted.

## UV Trivial Pursuit

► The heats of hydrogenation of conjugated dienes are directly related to their thermodynamic stabilities.

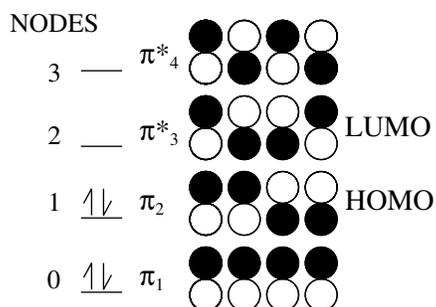
► A molar extinction coefficient of  $> 10,000$  is present in all conjugated compounds. ( $\pi, \sigma, \pi$ ), but absent in nonconjugated compounds.

► UV spec occurs when a photon elevates an electron from the **HOMO to the LUMO**.

► A change from a  $\pi$  to a  $\pi^*$  orbital represents an electronic transition from a bonding pi orbital to an antibonding pi orbital.

► In the ground state 1,3-butadiene has one nodal plane in the HOMO ( $\pi_2$ ) and two nodal planes in the LUMO ( $\pi_3^*$ ). See below.

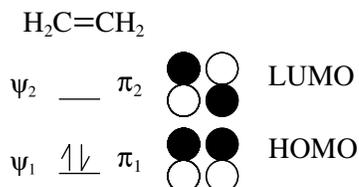
► The Molecular Orbitals of 1, 3-butadiene:



► On Dr. Snyder's tests, **conjugated compound's contain only  $sp^2$  hybridized atoms** (this is not true on the MCAT).

►  $\lambda_{\max}$  is the wavelength that is maximally absorbed by **UV spec**.

► For noncyclic conjugated systems  $\psi_1$  corresponds to  $\pi_1$ . therefore  $\psi_1$  is the highest occupied molecular orbital energy level for ethylene,  $\text{CH}_2=\text{CH}_2$ , in its ground state:



## NMR Trivia (H & C)

► Absorbs and releases energy by **nuclear spin inversion**.

► Peak **heights are irrelevant**, peak areas are relevant.

► 1,1-dimethylcyclopropane has 2 hydrogen signals and three carbon signals.

► 1,1-dimethylcyclobutane has 3 hydrogen signals and four carbon signals.

► A triplet and a quintet (not a pentet) is present in the H-NMR spectrum of  $\text{ClCH}_2-\text{CH}_2-\text{CH}_2\text{Cl}$ .

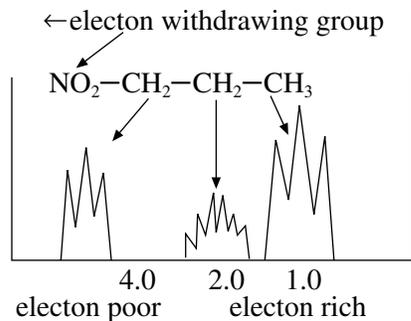
► A **triplet** (3 H's) and a **quartet** (2 H's) indicates an **ethyl group**.

► A doublet (6 H's) and a septet (1 H) indicate an isopropyl group.

► **Tetramethyl silane** *TMS* is a spectroscopic standard used to set the **zero point** on H-NMR.

► **Splitting patterns** result from **protons located on neighboring atoms** (H-NMR &  $^{13}\text{C}$ -NMR). (On the MCAT this also may occur in H-NMR from protons located on the same atom).

► Here's the H-NMR of 1-nitropropane:



► **H-NMR is best to tell the difference between an aldehyde and a ketone**, between an aldehyde has a signal at  $\delta$  9-10, and a ketone does not.

► **Due to a lower relative abundance of  $^{13}\text{C}$ ,  $^{13}\text{C}$ - $^{13}\text{C}$  splitting is not observed.** but  $^1\text{H}$ - $^{13}\text{C}$  and  $^1\text{H}$ - $^1\text{H}$  is.

► The H-NMR of all unsubstituted **cycloalkanes** consists of **one singlet**.