

CHE 173

Winter, 2005

Specific Objectives for Quiz 1

1. Know what spectroscopy is and have an understanding of the types of spectroscopy that are useful in the determination of organic structures.
1. Understand that the energy of a photon can be expressed in terms of frequency (ν) or wavelength (λ) and that energy is directly proportional to frequency and inversely proportional to wavelength; the higher the frequency, the greater the energy... the greater the wavelength, the lower the energy.
3. Be familiar with the electromagnetic spectrum and have a sense of the relative energies of different types of electromagnetic energy.
4. Understand that molecules are very selective with respect to the frequency of electromagnetic radiation (energy) they absorb; the energy absorbed must equal the difference in energy (ΔE) between two quantized energy states of a molecule (vibrational states for IR, electronic states for UV, and spin states for NMR).
5. Understand that the absorption of e.m. radiation by a molecule may be measured by a *spectrometer*, and that the relationship between frequency and absorption is plotted as a *spectrum* (appears as a series of "peaks" at characteristic frequencies).
6. Understand that IR spectroscopy measures the absorption of infrared (IR) radiation by a molecule; absorption of IR radiation by a molecule causes covalent bonds to vibrate (stretch or bend) with greater amplitude, and that different types of bonds absorb characteristic frequencies of IR radiation.
7. Be able to recognize absorption bands in an IR spectrum that represent specific types of bonds (see Table 13.4 in Carey or on your green sheet).
8. Understand that UV-VIS spectroscopy measures the absorption of ultraviolet or visible (UV-VIS) radiation by a molecule; UV-VIS energy is sufficient to cause an electronic transition; promotion of an electron from one orbital to a higher energy orbital, $p \rightarrow p^*$ or $n \rightarrow p^*$, which are generally possible for conjugated systems.
9. Understand that in UV-VIS spectroscopy, compounds with smaller HOMO-LUMO gaps require less energy for promotion of an electron and if the gap is small enough, compounds will absorb in the visible region and appear colored; remember that the greater the extent of conjugation, the smaller the HOMO-LUMO gap.
10. Understand that mass spectrometry (MS) measures what happens to a molecule when it is bombarded with a beam of high energy electrons... a molecular ion (an unstable radical cation species) is produced which fragments; positively charged

fragments are deflected through a magnetic field, separated according to mass/charge and detected as a mass spectrum (m/z vs. relative abundance).

11. Be able to recognize the molecular ion peak in a mass spectrum and understand that although it is typically of very low abundance, its m/z value corresponds to the molecular weight of the sample.
12. Be able to recognize which peak in a mass spectrum represents the "base peak" and be able to predict from a given molecular structure how the corresponding molecular ion is most likely to fragment.
13. Be able to recognize from a mass spectrum if a sample contains a bromine or chlorine atom.
14. Be able to distinguish from the mass spectrum whether a sample contains an odd number of nitrogen atoms (1, 3, 5, etc.) or an even number (0, 2, 4, etc.).
15. Be able to calculate the IHD ("index of hydrogen deficiency") value from a given molecular formula.

$$\text{IHD} = 1/2(2C + 2 - H - X + N)$$

Where, C = # carbon atoms

H = # hydrogen atoms

X = # halogen atoms

N = # nitrogen atoms

$$\begin{aligned}\text{So, for example, the IHD for } C_5H_5N \text{ is} &= 1/2 [2(5) + 2 - 5 - 0 + 1] \\ &= 1/2 (10 + 2 - 5 + 1) \\ &= 1/2 (8) = 4\end{aligned}$$

16. Understand what an IHD of "4" (or whatever) means.
17. Be able to derive possible molecular formula(s) from a given molecular weight (or from the m/z value of the molecular ion in a MS).
18. Understand that nuclear magnetic resonance (NMR) spectroscopy is a method for structure determination that is based on the effect of molecular environment on the energy required to promote a given nucleus from a lower energy spin state to a higher energy spin state.
19. Know that a ^1H NMR spectrum tells us about the environments of the various hydrogen atoms in a molecule.
20. Have a general sense of how ^1H NMR spectroscopy works:
 - (a) there are two possible spin states for an ^1H nucleus ($+1/2$ and $-1/2$) and in the absence of an applied magnetic field they are equal in energy.
 - (b) In the presence of an applied magnetic field, however, the two states are not of equal energy; nuclei aligned with the applied magnetic field are lower in energy than nuclei aligned against the field (see Figure 13.4)... how much lower depends on the strength of the applied field.

- (c) As long as the two spin states have different energy, it is possible for the sample to absorb electromagnetic radiation (in this case in the radio wave frequency).
 - (d) When the sample (in a magnetic field that is held constant, as in most modern NMR spectrometers) is subjected to a brief, intense pulse of radiation a "spin flip," or transition from the lower energy spin states to the higher energy spin states occur and the nuclei are said to be "in resonance."
 - (e) As the nuclei return to their original state, they emit an electrical signal in the receiver that decreases with time; the resulting Free Induction Decay (FID) data are the composite of the decay patterns of all the protons in the molecule.
 - (f) Finally, the FID pattern is converted from the "time domain" to the "frequency domain" into a **spectrum** by a mathematical process called *Fourier Transform*.
21. Understand that in NMR spectroscopy, the greater the applied magnetic field, the greater the difference in energy between the two spin states and the higher the frequency of absorption.
 22. Understand that the position in an NMR spectrum where a signal occurs is referred to as a *chemical shift* value; chemical shifts are usually expressed in terms of the delta scale (δ) in units of parts per million (ppm) from TMS as the reference (assigned a value of 0):

$$\text{chemical shift (ppm)} = \delta = \frac{\text{[distance downfield from TMS in Hz]}}{\text{[operating frequency of the spectrometer in MHz]}}$$
 23. Understand what is meant by "shielding" and the effect this has on chemical shift value in a proton NMR spectrum.
 24. Understand that a separate signal is seen in the ^1H NMR spectrum for each *chemically nonequivalent* proton in a molecule; be able to predict how many signals will be present in the ^1H NMR spectrum of a given molecule (see Carey Problem 13.9, for example).