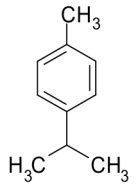
Strategies for Solving Problems using IR, ^{1}H-NMR and ^{13}C-NMR

1. First of all determine the Index of Hydrogen Deficiency (IHD)

   $IHD = \#C\ atoms - \frac{\#\ H\ atoms - 2}{2}$; Note: For each halogen atom in the molecular formula add one to the total hydrogen atoms in the molecular formula; for each nitrogen atom present in the molecular formula subtract one from the total hydrogen atoms. Example:

$C_5H_9O_2Br$	$IHD = 5 - \frac{10-2}{2} = 1$
$C_5H_{11}N$	$IHD = 5 - \frac{10-2}{2} = 1$

   Cases where the IHD ≥ 4 there is the **strong** possibility of a benzene ring. Chemical shifts (δ ≥ 6.5 ppm) on the ^{1}H-NMR will confirm the presence of the aromatic ring.



$C_{10}H_{14}$

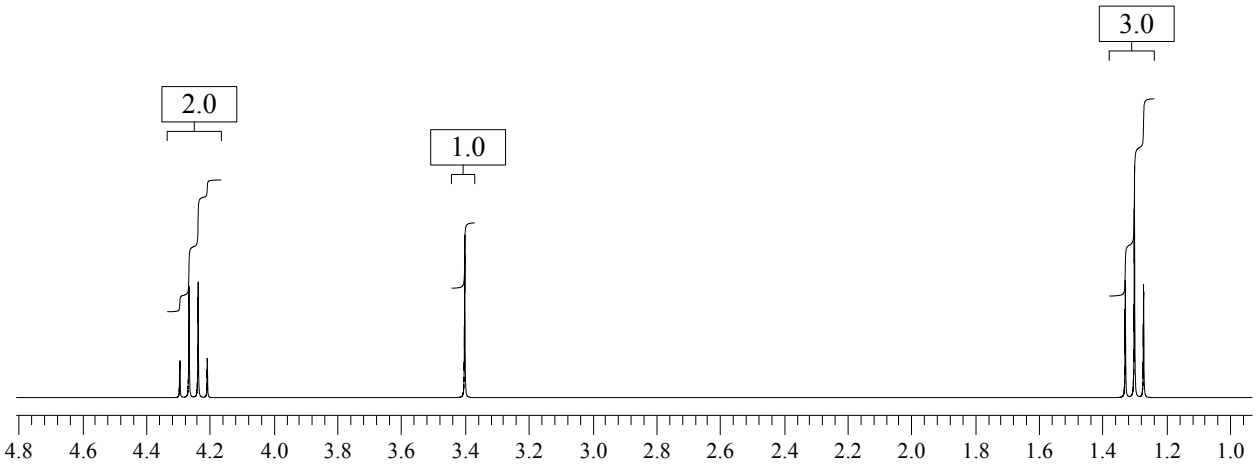
$IHD = 10 - \frac{14-2}{2} = 4$

2. If you are provided with the Infrared Spectrum (IR) of the compound look for functional groups.
   a) A molecule containing oxygen might show a broad signal around the 3300 cm^{-1} which suggests the presence of –OH due to an alcohol or carboxylic acid. Hydrogen-bonding of the –OH stretch makes this peak very broad. If, on the other hand, the molecule contains nitrogen and there's a medium intensity peak around 3300 cm^{-1} suspect an –NH stretch, i.e. the presence of an amine or amide.
   b) The very sharp absorption of the C=O around ~1625 to ~1750 cm^{-1} indicates the presence of a carbonyl compound; aldehydes, ketones, carboxylic acids, esters, amides.
   c) Functional groups like -C≡N (nitriles), -C≡C-H (alkynes) are easily identified in IR.

3. Use of ^{1}H-NMR.
   a) How many different sets of signal appear in the spectrum? (This can be determined by the number of integrated peaks.)
   b) What is the relative ratio of all the different hydrogen peaks present? Do they add to the total number of hydrogen atoms in the molecular formula? See Example below.

   The ^{1}H-NMR of the compound with molecular $C_7H_{12}O_4$ (shown above) has three different types of hydrogen atoms (there are three different integrated peaks) and an ***IHD = 2***. The ratio of hydrogen atoms do not add to the total hydrogen atoms. This is highly suggestive of symmetry. But multiplying by two the ratios becomes 4:2:6, which then add up to 12 total hydrogen atoms. The **chemical shift** provides information into the chemical environment of the different hydrogen atoms in the molecule. As a rule of thumb, a chemical shift seen at δ ≤ 1.0 ppm and an integration of 3.0 most probably indicates an alkyl group whose terminal is a –CH_3. An aldehyde proton will show at ~9.0 ppm and a carboxylic acid ~11.0 ppm. Remember that electronegative atoms tend to deshield hydrogen atoms moving their chemical shifts downfield by the inductive effect.

C7H12O4



c) The **splitting patterns** of each signal are very important because they can help us understand the hydrogen atoms attached to adjacent carbon atoms (about 3 bonds away).

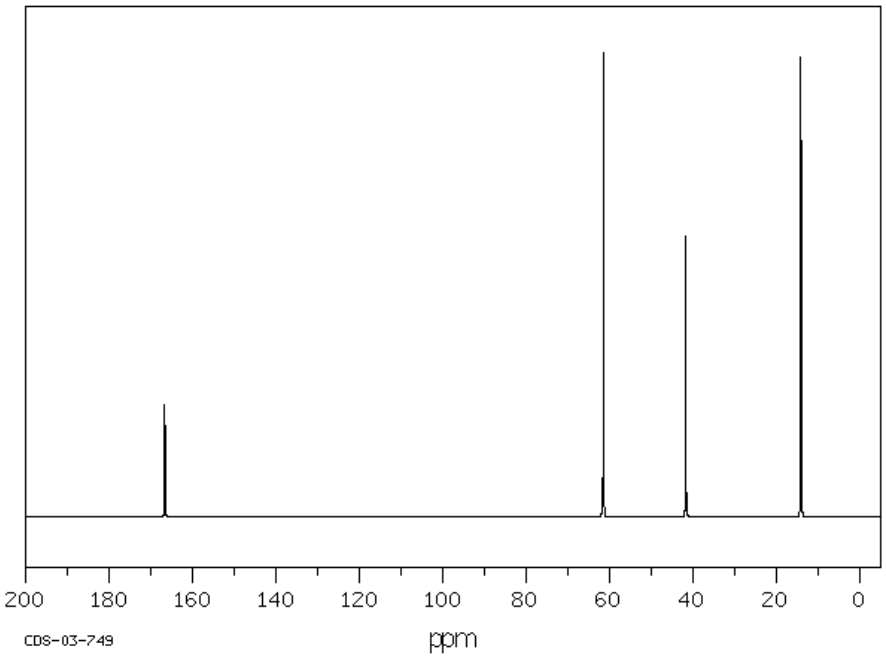
1. Remember the ***n+1*** rule for the splitting pattern.
2. An isolated ethyl group ($-CH_2CH_3$) will show a particular pattern. A ***triplet*** results from the $-CH_3$ (the neighbor is a $-CH_2-$) and a ***quartet*** from the $-CH_2-$ (see ^{1}H-NMR above).
3. An ***isolated*** isopropyl group ($-CH(CH_3)_2$) will show a ***doublet*** from the methyl groups and a ***septet*** from the methyne (-CH-).
4. The 1,4 di-substituted benzene is the simplest splitting pattern. It usually show up as a pair of ***doublets*** each with an integration of 2.

4. After assigning partial structures on the ^{1}H-NMR spectrum try to place them together to form the compound. Next, try to generate a spectrum from the proposed structure and compare it to the spectrum provided.

5. Use of ^{13}C-NMR

a) The proton-decoupled ^{13}C-NMR will show the different types of carbon atoms (non-equivalent sets of carbons) in the molecule. If the number of carbon signals is less than the number of carbon atoms in the molecule this is suggestive of symmetry in the molecule. (See sample below) Signals in the 160 – 220 ppm range are indicative of a carbonyl functional group (amides, ester, ketones, etc.)

$C_7H_{12}O_4$



Answer to the ^{1}H-NMR and ^{13}C-NMR above.