

Solving Spectroscopy Problems

The following is a detailed summary on how to solve spectroscopy problems, key terms are highlighted in bold and the definitions are from the illustrated glossary on Dr. Hardinger's website.

Introduction:

The first step is recognizing your M, M+1, and M+2 values. The m/z values increase by one as we go from M to M+1 because **M+1 is the molecular ion whose mass is one higher than M**. Likewise, the m/z value increases by two as we go from M to M+2 because **M+2 is the molecular ion whose mass is two higher than M**. Now that we know which m/z corresponds to which M value, we can use some basic steps to figure out the molecular formula of the molecule.

Step 1: Figure out the Number of Carbons

This step involves using the relative abundance value of your M+1 value. Before you use this number, make sure the relative abundance of your M value is set to 100%. If it isn't, make the necessary calculations to scale both your M as well as M+1 and M+2 so that the relative abundance of M is 100%.

Now that the relative abundance of M is 100%, we can use the fact that the natural abundance of Carbon 13 molecules is 1.107%. When we observed our M+1 value and recorded its relative abundance, we know that we are observing a molecular ion of M that is 1 amu heavier. Because protons must stay constant for a particular element and the weight of electrons is negligible, the additional weight must come in the form of additional neutrons. When we add or subtract a neutron we are creating isotopes of an element and these isotopes have different natural abundances. We know that the extra neutron is being added to the carbon 12s in the M values because the natural abundance of hydrogen is negligible. Thus, in the M+1 spectrum, we are observing the relative abundance of carbon 13 which is 1.1% after scaling M to 100%.

To solve for the number of carbons, we simply take the M+1 relative abundance and divide it by 1.1%. This gives the approximate number of carbons for the compound.

Example: Dr. Hardinger's Thinkbook Page 174 Problem 1

Mass spectrum: m/z = 106 (M; 100%), m/z = 107 (8.91%), and m/z = 108 (0.05 %).

The M+1 value is 107 since we know that the definition of M+1 is a molecular ion whose mass is one amu higher than M. 107 amu is one amu higher than the m/z of M so it must be the M+1 value. Dividing the relative abundance of M+1 (8.91%) by 1.1% gives 8.1. While we can say that there are 8 carbons in the compound, numerous practice problems have given integers on both extremes of the value. So to be safe, it is safe to assume that there are 8 or 9 carbons and use later data and experimentation to rule out the number of carbons.

Step 2: Look at M+2 Contributors

The second step is to see if there are any contributors in the M+2 spectrum. The only isotopes that have significant peaks in this spectrum are sulfur, chlorine, and bromine. By scaling M to 100% and finding the relative abundances of sulfur, chlorine, and bromine through their natural abundances of M versus M+2, we can determine the intensity ratio of M / (M+2).

Because sulfur, chlorine, and bromine have their own distinct intensity ratios, we can use this fact to identify whether or not these elements are present in the compound. The intensity ratio of M compared to M+2 for sulfur is 100:4.4. Thus the M+2 intensity ratio for a compound containing sulfur will be about 4.4%. The same rule can be applied to chlorine and bromine which yield intensity ratios of about 31.9% and 97.2% respectively.

Example: Dr. Hardinger's Thinkbook Page 174 Problem 1

Mass spectrum: $m/z = 78$ (M; 100%), $m/z = 79$ (3.42%), and $m/z = 80$ (32.6 %).

The M+2 has an m/z of 80 since the definition of M+2 is a molecular ion whose mass is amu higher than M. The relative abundance of M+2 is 32.6% in this compound which is very close to 31.9%. We can thus conclude that chlorine is present in this compound.

Step 3: Figure out the Molecular Formula

Now that we have the mass of the compound, possible number of carbons, and the presence of sulfur, chlorine, or bromine, we can put these together to figure out the molecular formula. In addition to the information we figured out in the previous steps, there are two other rules that are very helpful in determining the molecular formula.

The first is the nitrogen rule. **The nitrogen rule states that when m/z for M has an even mass (even number of amu), the corresponding molecular formula has an even number of nitrogen atoms (0, 2, 4, etc.) and when m/z for M has an odd mass (odd number of amu), the corresponding molecular formula has an odd number of nitrogen atoms (1, 3, 5, etc.).** The limitations to this rule is that it only applies when the compound we are looking at only has hydrogen, carbon, nitrogen, oxygen, fluorine, chlorine, bromine, or iodine. If there are other elements present, the rule may or may not apply.

Example: Mass spectrum: $m/z = 106$ (M; 100%), $m/z = 107$ (8.91%), and $m/z = 108$ (0.05 %).

The mass of M is 106 amu. We can conclude that the number of nitrogens in the compound has to be even.

Example: Mass spectrum: $m/z = 149$ (M; 100%), $m/z = 150$ (11.53%), and $m/z = 151$ (0.06 %).

The mass of M is 149 amu which is an odd number. According to the nitrogen rule, we can conclude that there must be at least one nitrogen present. The next possibility is 3 nitrogens, the next 5 and so on.

The second rule is figuring out how many hydrogens a compound can have based on the number of carbons. **The hydrogen rule states that for a molecule containing only hydrogen, carbon, oxygen, nitrogen, fluorine, chlorine, bromine, and iodine, the maximum number of monovalent atoms possible (max H) for a given number of carbons (C) and nitrogens (N) is given by the equation $\text{max H} = 2\text{C} + \text{N} + 2$.** This rule is extremely important for ruling out impossible molecular formulas for a given molecule.

A special case should be taken into account. There is no way to determine if fluorine or iodine is present in the compound. Because of this, assume these two are absent from the compound unless it is otherwise stated.

Now that we know the rules, we can apply them to find the molecular formula. There is a very methodical approach to doing this:

Step 1: Figure out the number of carbons.

Step 2: Determine the presence of sulfur, chlorine, or bromine.

Step 3: Subtract the mass of the number of carbons and any element present in the M+2 spectrum from the mass of the M isotope.

Step 4: Use the remaining mass to determine how many nitrogen, oxygen, and hydrogen are possible. This can be done using the nitrogen and hydrogen rule. Alternate between possible numbers of oxygen and nitrogen. Make sure the remaining hydrogens are a plausible number.

Step 5: Eliminate impossible formulas using the hydrogen rule to determine the maximum number of hydrogens for each proposed structure.

Example: Mass spectrum: $m/z = 106$ (M; 100%), $m/z = 107$ (8.91%), and $m/z = 108$ (0.05 %)

The M+1 value shows us that there is a possibility of eight or nine carbon atoms. The M+2 value does not correspond to any of the three elements that show significant peaks in the M+2 spectrum so we can conclude that sulfur, chlorine, and bromine are not present in the compound. The problem did not say there is fluorine or iodine so we can assume they are absent. The mass of M is 106 amu. If we assume there are eight carbons, then we subtract 8×12 from 106 which gives us 10 amu.

Oxygen	Nitrogen	Hydrogen	Formula	Notes
0	0	10	C_8H_{10}	Possible
1	0	-6	$\text{C}_8\text{H}_6\text{O}$	Not possible
0	2	-18	$\text{C}_8\text{H}_{18}\text{N}_2$	Not possible

This means we have 10 amu to fit in nitrogen, oxygen, and hydrogen. Since the mass of M is even, the nitrogen rule says that we can have 0, 2, 4, etc. number of nitrogens. The available amount of mass is too little to include nitrogen so we can say that there are zero nitrogens which agrees with the nitrogen rule. There is also not enough mass for the presence of oxygen so it can also be eliminated. The remaining 10 amu must then go to hydrogen resulting in a molecular formula of C_8H_{10} . To check if this is a valid formula, we need to check that the number of

hydrogen agrees with the maximum number of hydrogens possible: $2(8) + 0 + 2 = 18$. 10 is well under 18 so the formula is valid.

If we assumed there were nine carbons, then similarly the amount of mass we have to work with would be $106 - (9 \times 12) = -2$. Negative numbers of elements are not possible so we can conclude that there cannot be nine carbons.

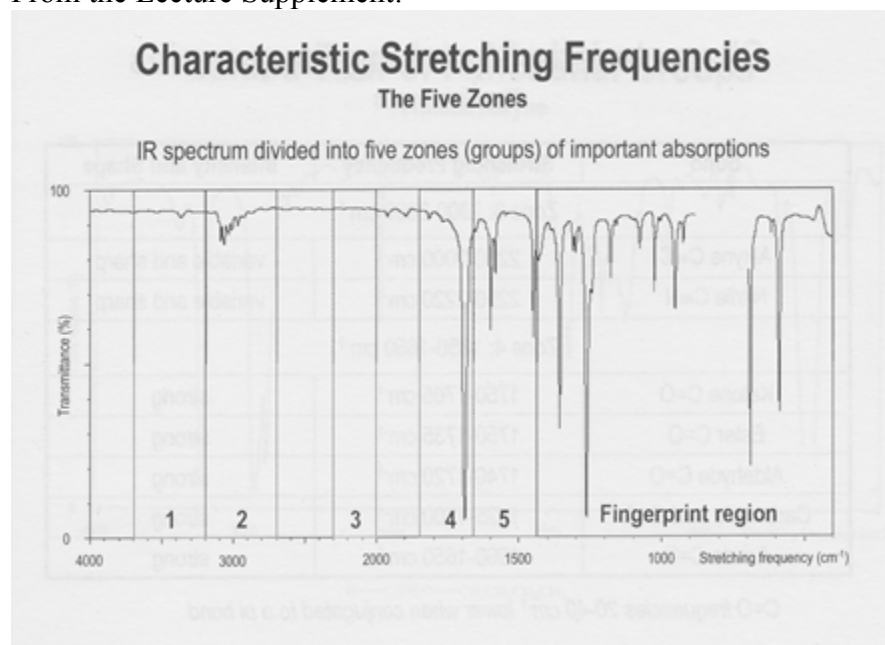
Oxygen	Nitrogen	Hydrogen	Formula	Notes
0	0	-2	C_9H_{-2}	Not possible

Step 4: Identifying Functional Groups

Just having the molecular formula is not enough when we are trying to figure out the structure of a compound. There are many possible isomers of a compound that are possible. The correct structure can be narrowed down by using infrared spectroscopy. **Infrared spectroscopy is the study and applications of infrared spectra and used mainly to determine the absence or presence of functional groups with a molecule.** Knowing the presence or absence of a functional group gives lots of insight into the structure of a molecule and is a huge step in determining structure.

Before we can identify functional groups, we need to know how to read an infrared spectroscopy graph.

From the Lecture Supplement:



An infrared spectrum is divided into five regions, six if you are including the fingerprint region. Each region has distinct peaks that correspond to the possible presence or absence of functional groups. Many functional groups have peaks that occur in more than one zone. While

peaks show the presence of a functional group, we need to also consider the width of the peak. Some functional groups create broader peaks than others in the infrared spectrum.

The table from Dr. Hardinger's Lecture Supplement Page 118-119 gives an excellent map of what to look for in each zone when determining the presence of functional groups.

Alcohol: look for peaks between 3650 cm^{-1} and 3200 cm^{-1} , peaks should be strong and broad

Terminal Alkyne C-H: look for peaks between 3340 cm^{-1} and 3250 cm^{-1} , peaks are usually strong and sharp

Amine or Amide : look for peaks between 3500 cm^{-1} and 3200 cm^{-1} , peaks are medium and often broad

Aryl or Vinyl C-H: look for peaks between 3100 cm^{-1} and 3000 cm^{-1} , peaks are variable

Alkyl: peaks between 2960 cm^{-1} and 2850 cm^{-1} , easy way is to see if there peaks from 3000 cm^{-1} to the end of zone 2, peaks are variable

Aldehyde: look for peaks between 2900 cm^{-1} and 2700 cm^{-1} as well as between 1740 cm^{-1} and 1720 cm^{-1} , peaks are medium

Carboxylic Acid: look for peaks between 3000 cm^{-1} and 2500 cm^{-1} as well as between 1725 cm^{-1} and 1700 cm^{-1} , peaks are usually very strong and may be broad

Alkyne: look for peaks between 2260 cm^{-1} and 2000 cm^{-1} , peaks are variable and sharp

Nitrile: look for peaks between 2260 cm^{-1} and 2220 cm^{-1} , peaks are variable and sharp

Ketone: look for peaks between 1750 cm^{-1} and 1705 cm^{-1} , peaks are strong

Ester: look for peaks between 1750 cm^{-1} and 1735 cm^{-1} , peaks are strong

Amide: look for peaks between 1690 cm^{-1} and 1650 cm^{-1} , peaks are strong

Alkene: look for peaks between 1680 cm^{-1} and 1620 cm^{-1} , peaks are variable

Characteristic Stretching Frequencies
The Five Zones

Bond	Stretching Frequency	Intensity and Shape
Zone 1: $3700\text{--}3200\text{ cm}^{-1}$		
Alcohol O-H	$3650\text{--}3200\text{ cm}^{-1}$	usually strong and broad
Alkyne $\equiv\text{C-H}$	$3340\text{--}3250\text{ cm}^{-1}$	usually strong and sharp
Amine or amide N-H	$3500\text{--}3200\text{ cm}^{-1}$	medium; often broad
Zone 2: $3200\text{--}2700\text{ cm}^{-1}$		
Aryl* or vinyl** $\text{sp}^2\text{ C-H}$	$3100\text{--}3000\text{ cm}^{-1}$	variable
Alkyl $\text{sp}^3\text{ C-H}$	$2960\text{--}2850\text{ cm}^{-1}$	variable
Aldehyde C-H	$\sim 2900, \sim 2700\text{ cm}^{-1}$	medium; two peaks
Carboxylic acid O-H	$3000\text{--}2500\text{ cm}^{-1}$	usually strong; very broad
Zone 3: $2300\text{--}2000\text{ cm}^{-1}$		
Alkyne C=C	$2260\text{--}2000\text{ cm}^{-1}$	variable and sharp
Nitrile C=N	$2260\text{--}2220\text{ cm}^{-1}$	variable and sharp
Zone 4: $1850\text{--}1650\text{ cm}^{-1}$		
Ketone C=O	$1750\text{--}1705\text{ cm}^{-1}$	strong
Ester C=O	$1750\text{--}1735\text{ cm}^{-1}$	strong
Aldehyde C=O	$1740\text{--}1720\text{ cm}^{-1}$	strong
Carboxylic acid C=O	$1725\text{--}1700\text{ cm}^{-1}$	strong
Amide C=O	$1690\text{--}1650\text{ cm}^{-1}$	strong
Zone 5: $1680\text{--}1450\text{ cm}^{-1}$		
Alkene C=C	$1680\text{--}1620\text{ cm}^{-1}$	variable
Benzene C=C	$\sim 1600\text{ cm}^{-1}$ and $\sim 1500\text{--}1450\text{ cm}^{-1}$	variable; 1600 cm^{-1} often two peaks

Benzene Ring: look for two peaks in Zone 5 at around 1600 cm^{-1} and around 1500 cm^{-1} , peaks are variable

Now that we know how to spot out functional groups when we are presented with a graph of the infrared spectrum, we need to be able to determine which functional groups are possible and which ones aren't for a given compound. Because some peaks can mask or hide other peaks, it is useful to have a general idea of what to look out for when trying to determine the functional groups. There are two ways to do this: looking at the molecular formula and figuring out the DBE also known as the double bond equivalent.

By looking at the molecular formula, we can determine if there is the possibility of any carbonyl functional groups in the molecule if the molecular formula contains oxygen. We can also determine if some functional groups such as an alcohol group or amide are even possible for the given molecule.

By using DBE, we can determine the number of pi bonds or benzene rings present in the molecule. **The DBE is calculated by $C - (H/2) + (N/2) + 1$.** The value derived from the DBE corresponds to the possible bonds available to the molecule. One DBE means there is a possibility of one ring or one pi bond. Two DBE means there are two pi bonds, two rings, or one of each. Four DBE means there is a possibility of a benzene ring, four pi bonds, or four rings. By calculating the DBE, we can anticipate the types of bonds and functional groups we should expect to see in the infrared spectrum.

Like mass spectroscopy, there is a very methodical way of spotting functional groups using infrared spectroscopy:

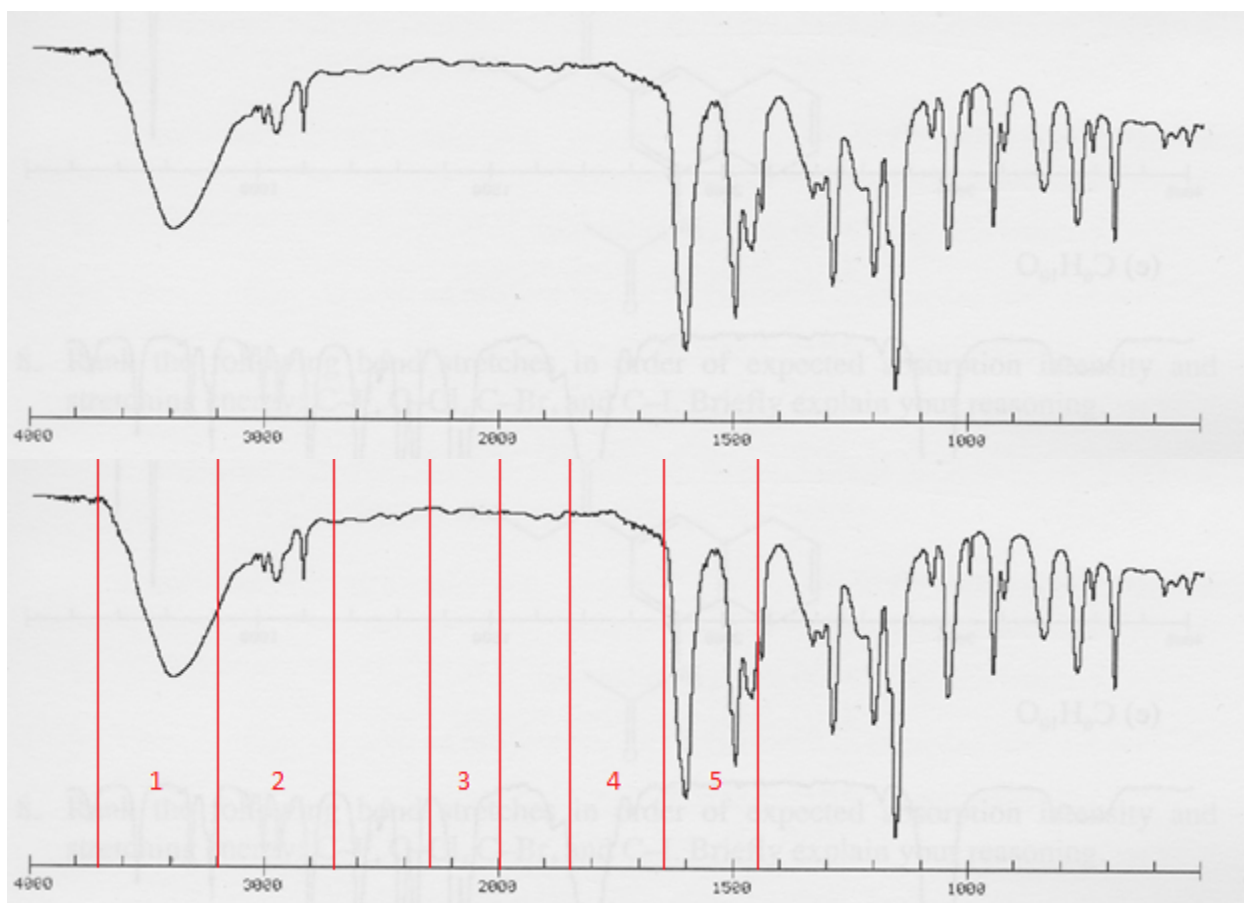
Step 1: Calculate the DBE

Step 2: Look at the molecular formula to get an idea of what functional groups will be possible.

Step 3: Analyze each of the five zones for the presence of peaks that correspond to functional groups. Remember that some functional groups have peaks in more than one zone.

Example: Dr. Hardinger's Thinkbook Page 137 Problem 5a.

Perform a Five-Zone Analysis for the following IR Spectra: $C_7H_8O_2$



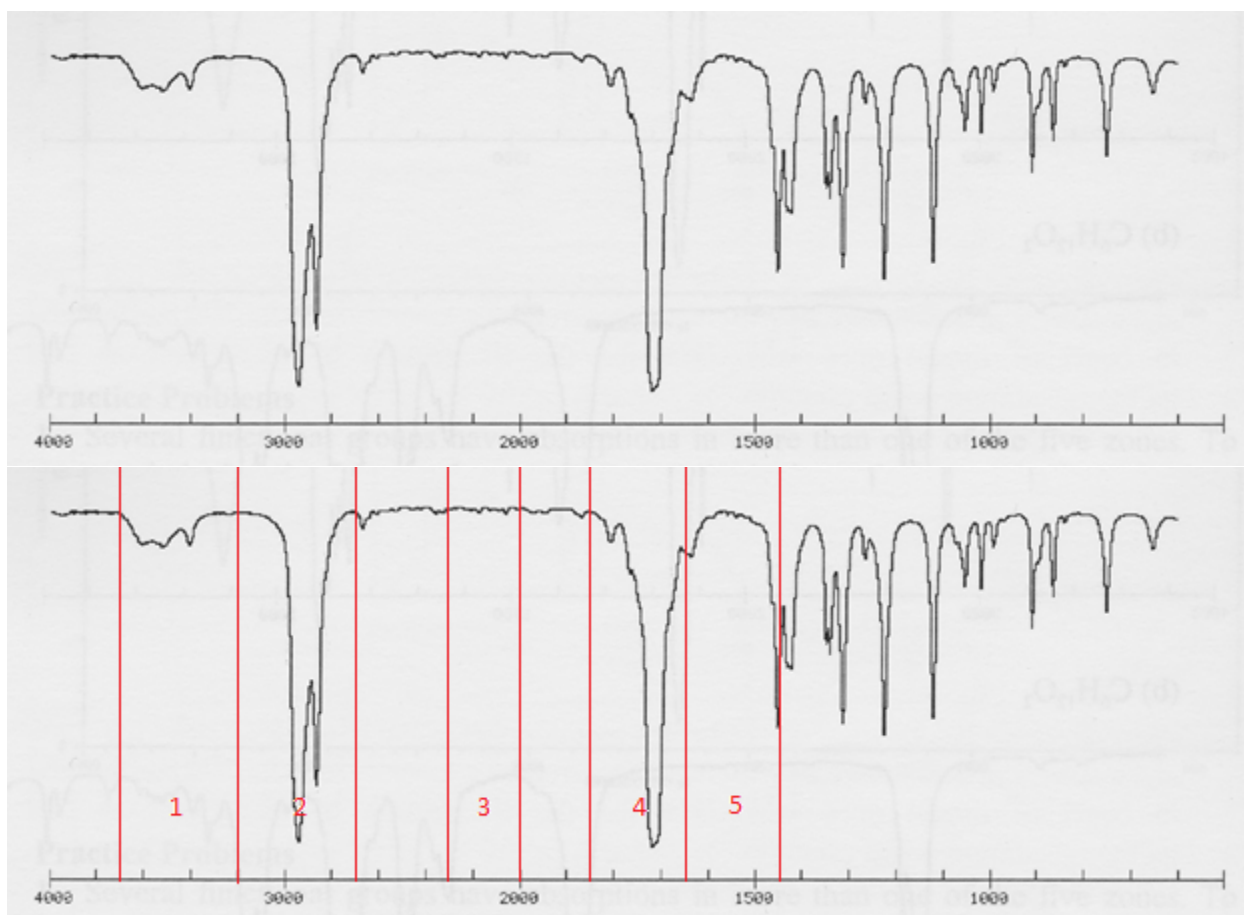
The first step is to calculate the DBE. The DBE is equal to $7 - (8/2) + 1 = 4$. There are four pi bonds, four rings, or a possible benzene ring.

The next step is to look at the molecular formula. There are two oxygens so functional groups containing oxygen are a definite possibility.

We can now perform a five zone analysis. Let's start with Zone 1. Zone 1 contains one peak that is pretty strong and very broad. The stretching frequency fits alcohol and there is an oxygen in the molecular formula so there is definitely an alcohol present. An amine or amide is not possible because the formula does not have any nitrogens. Alkynes are not possible because there is no peak in Zone 3. In Zone 2, we have some very small peaks both before and after 3000 cm^{-1} . This means that there are vinyl or aryl C-H bonds and alkyl C-H bonds. There are no strong peaks in Zone 2 so there can't be an aldehyde or carboxylic acid. This is further reinforced by the absence of any peaks in Zone 4. Zone 3 and Zone 4 have no peaks so we can now move onto Zone 5. We see two significant peaks in Zone 5, one at 1600 cm^{-1} and the other at around 1500 cm^{-1} . This matches the two peaks required for a benzene ring. A benzene ring takes up four DBE so we are left with zero DBE. Thus, it is impossible for there to be another alkene in Zone 5 because we are out of DBE.

Example: Dr. Hardinger's Thinkbook Page 174 Problem 5e.

Perform a Five-Zone Analysis for the following IR Spectra: $\text{C}_6\text{H}_{10}\text{O}$



The first step is to calculate the DBE. The DBE is equal to $6 - (10/2) + 1 = 2$. There are two pi bonds or 2 rings.

The next step is to look at the molecular formula. There is an oxygen so functional groups containing oxygen are a possibility.

We can now perform a five zone analysis. Let's start with Zone 1. Zone 1 has no significant peaks. There is definitely not an amine or amide group since there are no nitrogens in the formula. Zone 2 only has peaks after 3000 cm^{-1} so we can conclude that there are alkyl C-H. There are no peaks before 3000 cm^{-1} in zone 2 so there are no vinyl or aryl C-H. There is a peak at 2900 cm^{-1} for an aldehyde but there is no corresponding peak at 2700 cm^{-1} so an aldehyde functional group is not present. There is a peak around 3000 cm^{-1} which could mean a carboxylic acid, however, there is only one oxygen and carboxylic acid requires two. There are no peaks in Zone 3 so we can eliminate the possibility of an alkyne or nitrile. There is a strong peak in Zone 4 which corresponds to a carbonyl functional group. We have already eliminated an aldehyde and carboxylic acid so the two remaining carbonyls are a ketone and an ester. There are not enough oxygens for an ester as it requires two and there is only one oxygen in the molecular formula. The only functional group that satisfies both the infrared spectrum as well as the molecular formula is a ketone. There are no significant peaks in Zone 5 so we can eliminate the

possibility of a benzene ring or alkene. In addition, there are not enough DBE for a benzene ring and the ketone in Zone 4 uses up the two DBE so there is not enough DBE for an alkene.

Step 5: Use $^1\text{H-NMR}$ Spectroscopy to Determine Structure

Now that we have the information from mass and infrared spectroscopy, we still do not have a concrete idea of the structure of the molecule. The best way to determine structure is through $^1\text{H-NMR}$ spectroscopy **which is the spectroscopic technique in which molecular structure is determined by examining the energy required for nuclear spin flip**. The energy required for a spin flip can give us valuable information on the conditions of a nucleus' field strength. This information gives us insight into the chemical structure of a molecule.

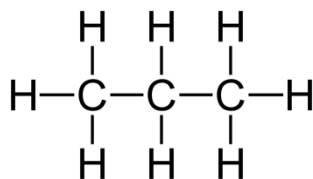
The information from $^1\text{H-NMR}$ can tell us the number of signals, position of the signals, the relative intensity of the signals, and the splitting of signals. We will examine each of these below.

Number of Signals:

The signal produced by $^1\text{H-NMR}$ is a result of photon absorption. The photon's energy is controlled by the magnetic environment around the nucleus. Thus, nuclei of the same magnetic environment will produce equivalent photon energy so there will only be one $^1\text{H-NMR}$ signal. Likewise, nuclei of different magnetic environments will produce photons of different energy which creates multiple $^1\text{H-NMR}$ signals.

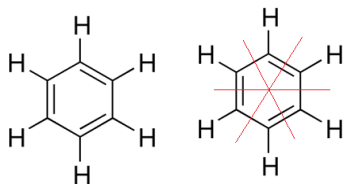
The next step to understanding the number of signals is to be able to determine which nuclei magnetic environments are the same and which ones are different. In order to be equivalent, the magnetic environments have to be completely identical. Because of this stringent rule, it is much easier to prove that magnetic environments are nonequivalent.

When we are determining equivalency, we are looking at the protons of the molecule. The proton in this case is hydrogen. Protons that are equivalent will share the same magnetic environment. The easiest way to understand this is to look at the structure of propane given below:



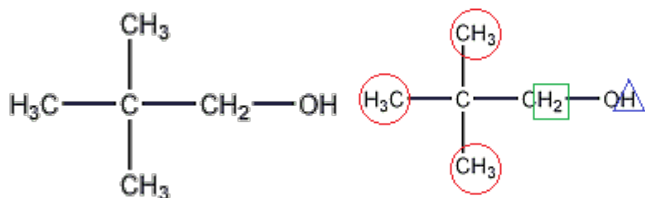
There are eight hydrogens in total. While each carbon is bonded to two or three hydrogens, not all of the hydrogens share the magnetic environment. The three hydrogens of the methyl group on the left share one magnetic environment, the two hydrogens of the middle methylene share another magnetic environment, and the three hydrogens of the methyl group on the right share the same magnetic environment as the other methyl group on the left. The

reasoning behind this is that the hydrogens of different types of group can never be in the same magnetic environment. Replacing the hydrogen in a methyl group with a carbon to make a methylene causes the hydrogens to be more deshielded because carbon is more electronegative than hydrogen. This increase in deshielding contributes to a different magnetic environment. Although the two methyl groups are located on opposite sides of the molecule, they share the same magnetic environment because their position relative to the middle methylene group is the same. In other words, symmetry can be used as a technique to identify proton equivalency or lack of. This can be seen in benzene below:



By drawing lines of symmetry through benzene, we can see that each hydrogen is symmetrical to the one straight across from it. Doing this around the benzene ring shows that every hydrogen shares the same magnetic environment as the others.

Let's look at one more example:



To determine the number of signals, we need to start by finding which protons are not equivalent. If we draw a horizontal line through the molecule, we can see that the top and bottom methyl groups are equivalent. In addition, the two hydrogens of the methylene are symmetrical and thus equivalent. However, the hydrogens of the methyl group are not the same as the hydrogens of the methylene because they do not share symmetry and they are from two different groups. The methyl group to the very left may not seem equivalent to the other two methyl groups but because of bond rotations about the carbon atom it is attached to, all three methyl groups appear equivalent. This leaves the hydrogen attached to the oxygen. This proton does not share any symmetry with the other protons and thus has a magnetic environment unique to itself. The result is three different magnetic environments for a total of three different signals.

Position of Signals:

The position of signals, also known as the chemical shift, gives insight into the nature of the proton. The amount of chemical shift is a result of the magnetic field strength at the nucleus in question. This field strength is greatly influenced by electronegativity. In general, the greater the electronegativity of the atom attached to the hydrogen or proton, the greater the hydrogen is deshielded because electron density is being pulled away from the hydrogen to the more

electronegative atom. This increase in deshielding is attributed to a higher chemical shift. The amount of chemical shift can tell us the structure of the groups attached to the proton as different groups have their own chemical shift patterns. A useful chemical shift pattern to understand is $RCH_3 < RCH_2R < R_3CH$. This is because a hydrogen is being replaced with an R group which is more electronegative than the hydrogen itself. The result is an increase in deshielding in the remaining hydrogens which increases the chemical shift.

While chemical shifts can give us clues on what the 1H -NMR peaks are, they are not a definite identifier and you should never identify a 1H -NMR peak solely on chemical shifts.

Relative Intensity of Peaks:

Another nice tool we can use to figure out the structure of a molecule from 1H -NMR information is integration. Because the amount of radio wave energy is proportional to the peak area in an 1H -NMR graph, measurements of these areas tell us the relative intensities of the 1H -NMR signals. By finding the relative intensities of the 1H -NMR signals, we can determine the relevant number of equivalent protons. The end result is that we have the intensity or number of equivalent protons relative to other protons that are equivalent to each other. This information comes in the form of a ratio that can then be used to figure out the actual number of equivalent protons.

Example: Dr. Hardinger's Lecture Supplement Page 146



3.55 ppm: integral = 1.0, hydrogen =

3.39 ppm: integral = 1.5, hydrogen =

Because integrals do not tell us how many hydrogens there are in every peak but rather the ratio of hydrogens compared to other peaks, we need divide up the total number of hydrogens and assign them to each peak so that the actual ratios agree with the integral ratios. To do this, we need to determine how many hydrogens to assign to every integral value of 1. The first step is to add up the integral numbers for every peak, $1.0 + 1.5 = 2.5$.

Now that we have our total ratio, we need to figure out how many hydrogens to assign to every integral value of one. To do this, we divide the total number of hydrogens (10) by the total ratio of 2.5. This gives us 4 hydrogens per one unit of integral. We use this information to figure out how many hydrogens each peak has. The first value has an integral value of 1, so $1 \times 4 = 4$ hydrogens. The second peak of integral 1.5 is also multiplied by 4 and we get 6. To check our work, we can see that the ratio of the actual number of hydrogens 4:6, is equivalent to the original integral ratio we were given of 1.0:1.5.

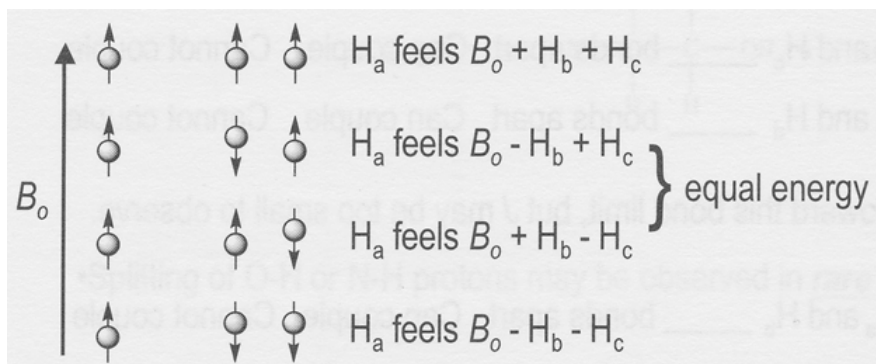
Signal Splitting:

Signal splitting can tell us a great deal about the environment around the nuclei of a molecule. When a nucleus only has one magnetic environment it causes one peak on the 1H -NMR spectrum known as a singlet. However, when this nucleus has more than one magnetic

environment such two, three, or four magnetic environments, it causes more than one peak to show up.

The reason behind this is the orientation of the charged particles. Let's look at a nuclei that only has one neighbor. When an external magnetic field is applied, the particles can be parallel to the field or antiparallel. Antiparallel is still parallel, it is just facing the opposite direction. Because of these two spin directions, the spin flip energy can either increase because the particles are pointing in the same direction as the external magnetic field or it can decrease because the antiparallel particles are counteracting the magnetic field. The result is two chemical shifts that are different and produces two peaks on the $^1\text{H-NMR}$ spectrum. The signal is then interpreted as a doublet.

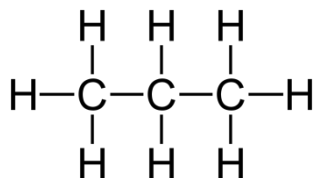
When there is more than one neighbor, we have to consider the effect of the alignment of the other protons. Similar to one neighbor, the protons can either be parallel or antiparallel. Let's consider a nuclei that has two neighbors. Each of the neighbors can be either parallel or antiparallel. There are three possibilities, each neighbor can either both add on to the external magnetic field, both subtract from the magnetic field, or one can add to and the other subtract from the magnetic field. This is illustrated in Dr. Hardinger's Lecture Supplement Page 150 below:



There are now three distinct chemical shifts so the original signal is split into three peaks and is known as a triplet.

While we can use this technique of figuring out the possible combinations of parallel and antiparallel protons, the combinations start to get complicated as the number of neighboring nuclei increases. Instead, we can look at a general trend. For example, when the nuclei had no neighbors, it produced a singlet because it only had its own magnetic environment to worry about. When the nuclei had one neighbor, it produced a doublet, and when it had two neighbors it produced a triplet. The trend is that **the signal for a proton with n neighbors is split into $n+1$ lines.**

Now that we know the trend to look for, all of this is useless if we don't know how many neighbors a nuclei has. There are a few rules when determining the number of neighbors a nuclei has. The first is that only nonequivalent protons couple. Let's look at propane:



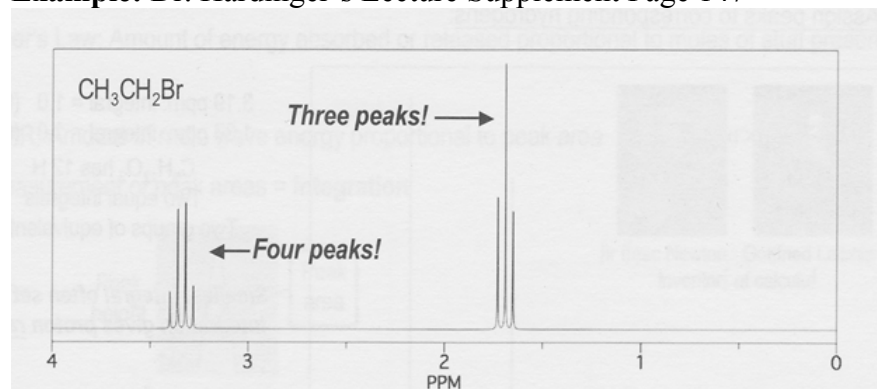
The hydrogens of the methyl group on the left can only couple with the methylene group next to it because it is the only neighbor that is not equivalent. All three hydrogens of the methyl are equivalent because of bond rotation so there can be no proton-proton spin coupling. The hydrogens of the methylene share a different magnetic environment because they are of a different group where the hydrogens are more deshielded because of the replacement of the hydrogen with a carbon. Therefore, the hydrogens of the methyl can't couple with each other but can couple with the two hydrogens of the methylene group and have two neighbors. We can expect the number of lines for the corresponding hydrogen peak to be three.

In the previous example, you may have asked why the hydrogens of the methyl group on the left did not couple with the hydrogen groups of the methyl group on the right. After all, these groups share the same magnetic environment. However, they do not follow the second rule of signal coupling. The second rule states that **protons separated by more than three single bonds usually do not couple**. In our propane example, any hydrogen that is further than the methylene group would be four single bonds so it would not be able to couple with the hydrogen of its similar methyl group on the other side of the molecule.

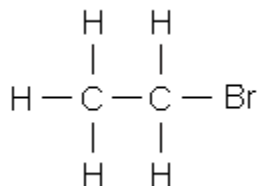
There are some exceptions and things to look out for with this rule. The first is that pi bonds do not count towards the single bond limit. These pi bonds act as a free spacer between the single bonds. The second is that benzene ring also acts as a free spacer. Because every hydrogen is within three single bonds of each other, every proton of benzene can couple with each other. However, other protons cannot couple with benzene, even if they are nonequivalent and within three single bonds of it. This is because benzene blocks the coupling of other protons.

The last rule is that **signals for O-H and N-H are usually singlets**. This is due to the fact that the nitrogen and oxygen typically carry lone pairs and are bound to another carbon. This isolates the hydrogens of the nitrogen and oxygen to their own magnetic environment and creates a single line.

Example: Dr. Hardinger's Lecture Supplement Page 147



The first step is to assign the peaks to the corresponding hydrogens. A diagram of the molecules helps a lot.



The hydrogens of the methyl group are all equivalent and share two neighbors, the hydrogens of the methylene group. We then expect there to be a triplet for this hydrogen group. The hydrogens of the methylene group are both equivalent to each other and have three neighbors, the hydrogens of the methyl group. We expect the signal to be a quartet for the methylene hydrogens. The hydrogens of the methylene are more deshielded because the carbon that has replaced the hydrogen in methyl is more electronegative than hydrogen and is drawing electron density away from the hydrogen. Also, the methylene group is closer to bromine which is electronegative. Chemical shifts decrease with distance so we can expect the methyl group to have a lower chemical shift. We can expect that the methylene hydrogens will have a higher chemical shift than the hydrogens of the methyl. When we look at the graph, we can see that our assumptions are correct as the chemical shift patterns match up with the number of peaks.

Step 6: Combining Everything in NMR

^1H -NMR gives an immense amount of information on the structure of a molecule. To be able to derive the final structure, we have to be able to put this information together. The easiest way to do this is to copy the ^1H -NMR data we are given onto a table.

Example: Dr. Hardinger's Thinkbook Page 159 Problem 8a.

Propose a structure for the compound: $\text{C}_6\text{H}_{12}\text{O}$; ^1H -NMR: 2.58 ppm (septet; integral = 1), 2.45 ppm (quartet; integral = 2), 1.07 ppm (doublet; integral = 6), and 1.01 ppm (triplet; integral = 3).

The first thing to do is to organize the information into an organized table.

Shift	Splitting	Integral	#H	Implications
2.58 ppm	septet	1		
2.45 ppm	quartet	2		
1.07 ppm	doublet	6		
1.01 ppm	triplet	3		

Now that everything is organized into a table, we can start filling in the blank spaces. The number of hydrogens is figured out using integration. We add up the total number of integrals which gives us our total ratio: $1 + 2 + 6 + 3 = 12$. We then compare this total ratio to the number

of hydrogens in our original formula which is 12. Therefore, we know that for every one unit of integral, there is one hydrogen. We can now fill in the #H column.

Shift	Splitting	Integral	#H	Implications
2.58 ppm	septet	1	1	
2.45 ppm	quartet	2	2	
1.07 ppm	doublet	6	6	
1.01 ppm	triplet	3	3	

To check that the number of our hydrogens is correct, make sure all the ratios of the hydrogens are the same as the ratios of the integrals. In this case, the check is simple since the number of integrals corresponded to the number of hydrogens.

The next step is to fill in the implications column. The best way to do this is to use information from the splitting and #H column. The information from the splitting pattern tells us how many neighbors each group has.

For example, the septet group has six neighbors around its nuclei since $n-1 = 7-1 = 6$. We know that there is one hydrogen in this group from our previous data so it has to be a methine since the other possibility of an alcohol is eliminated because hydrogens of alcohol groups typically produce singlets. Now, there are several possibilities for the methine. Because the methine needs to have six neighbors, it can be in the middle of two methyl groups, be attached to another methine, methylene, and methyl group, or it can be bounded to three other methylene groups. The best way to determine the best choice is whichever possibility has the least number of atoms. The first possibility has 10 atoms, the second has 11 atoms, and the third also has 11. Therefore, the first possibility is the best and we can proceed to write it into our implication column.

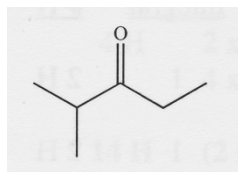
We can now turn our attention to the next group. The splitting is a quartet so we know the group needs to have three neighbors. There are two hydrogens which can be configured on one carbon or two carbons. In other words, since we have two hydrogens to work with, we can either produce a methylene or two methines. The possible combinations for a methylene are a methylene bonded to a methyl and a methylene bonded to another methylene and a methine. The possible combinations for a methine are a methine bonded to a methyl (remember that we have two methines so there would be two instances of a methine bonded to a methyl), a methine bonded to another methine and a methylene, and a methine bonded to three methines. The choice that uses the least number of atoms is the methylene bonded to the methyl so this is the most probable choice.

Shift	Splitting	Integral	#H	Implications
2.58 ppm	septet	1	1	CH in $\text{CH}(\text{CH}_3)_2$
2.45 ppm	quartet	2	2	CH_2 in CH_2CH_3
1.07 ppm	doublet	6	6	2 X CH_3 in CH_3CH
1.01 ppm	triplet	3	3	CH_3 in CH_3CH_2

Similar methods can be done for the other two groups to finish the table.

Now that we have our pieces, we need to check if they account for the entire molecule. Adding up all the pieces in the implications column gives us C_5H_{12} . This is one carbon and one oxygen short of the molecular formula we were given. This missing piece is actually clear if we had calculated the DBE to find out what type of bonds are present. The DBE is $6 - (12/2) + 1 = 1$. Therefore, there is one ring or one pi bond present. When we combine this information with the fact that we have an oxygen and carbon unaccounted for, it is fairly obvious that the carbon and oxygen must form carbonyl since the data from our table does not contain any double bonds.

The next step is to assemble all the pieces we found. We have a carbonyl, a methine, a methylene, and three methyls: two belong to the same group and the other is in its own group. The next steps are a combination of trial and error as well as recognizing the splitting patterns and how they must line up. The methyl group that has triplet splitting pattern must be located next to the methylene because it has two neighbors. We can verify this by looking at the splitting pattern of the methylene group which is a quartet which means it has three neighbors. The only way to make this splitting pattern true is to place the carbonyl next to the methylene. The carbonyl group does not contain any neighbors for the protons of the methylene to couple with so the 3 protons of the methyl group are the only ones it can couple with. This now leaves us with the methine and the two methyl groups. The methine has a splitting pattern of 7 so it must have 6 neighbors. The only place we can continue to attach molecules is to the carbonyl which will provide no neighbors for nearby groups to couple with. The only way for the methine to have 6 neighbors is to be bonded to the two methyl groups and the carbonyl. The resulting splitting patterns all agree with each other and our final structure is:

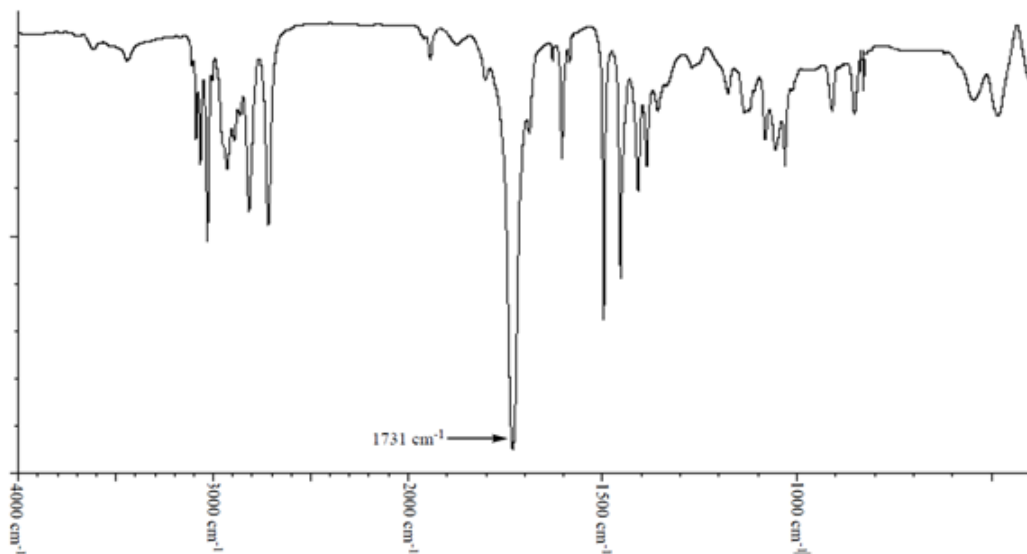


Step 7: Repeat

Solving spectroscopy problems is all about repetition and practice so let's consider another problem from Winter 2012 Exam 2 Problem 16.

Deduce the structure that corresponds to the spectral data

Mass spectrum: $m/z = 282$ (M; 100%), $m/z = 283$ (15.8%), and $m/z = 284$ (98 %). No fluorine or iodine



Shift	Splitting	Integral	#H	Implications
9.52 ppm	singlet	1		
7.40-7.27 ppm	multiplet	5		
4.71 ppm	triplet	1		
2.33 ppm	doublet	2		
1.58 ppm	quartet	4		
0.90 ppm	triplet	6		

Step 1: Figure out the Number of Carbons

The relative percentage of M+1 is 15.8%. We divide this by 1.1% to get 14.36. We can therefore have 14 or 15 carbons in our molecule.

Step 2: Look at M+2 contributors

The relative percentage of M+2 is 98% which is very similar to the observed relative percentage of bromine. We can conclude that bromine is present in the molecule.

Step 3: Figure out the Molecular Formula

The problem tells us there is no fluorine or iodine present so we can assume they don't exist. Let's start with the possibility of 14 carbons. This would give us $282 - (14 \times 12) - 79 = 35$ amu to work with. The nitrogen rule says that there must be an even number of nitrogen atoms since our M mass is even. The possible combinations of molecular formulas is summarized below:

Oxygens	Nitrogens	Hydrogens	Formula	Notes
0	0	35	$C_{14}H_{35}Br$	Not possible due to hydrogen rule
1	0	14	$C_{14}H_{19}BrO$	Possible
2	0	3	$C_{14}H_3BrO_2$	Not enough hydrogens
0	2	7	$C_{14}H_7BrN_2$	Not enough hydrogens

Other possibilities yielded negative mass which is not possible. The best formula is $C_{14}H_{19}Br$. However, we still need to consider the case with 15 carbons. 15 carbons would leave us with 23 amu to work with.

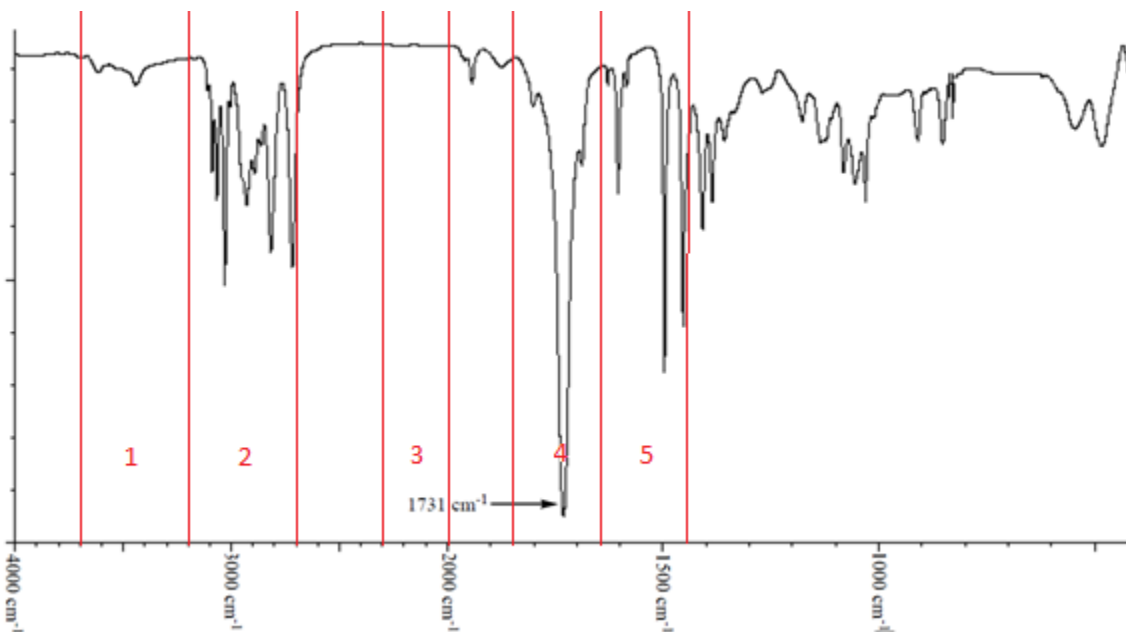
Oxygens	Nitrogens	Hydrogens	Formula	Notes
0	0	23	$C_{15}H_{23}Br$	Possible
1	0	7	$C_{15}H_7BrO$	Not enough hydrogens

The first possibility is possible if we only look at the mass spectroscopy data. However, looking at the infrared data shows that there is a carbonyl present. We can therefore eliminate the possibility of 15 carbons and we can conclude that our molecular formula of $C_{14}H_{19}BrO$ is correct.

Step 4: Perform a Five Zone Analysis

First calculate the DBE = $14 - (19+1)/2 + 1 = 5$. There are five pi bonds, or five rings, or a possible benzene rings, or combinations of all of the above.

Next, let's perform a five zone analysis.



There are no significant peaks in Zone 1 so we can tell that the oxygen in the formula is not a result of an alcohol group. There is no possibility of an amine or amide since there are no nitrogens in the formula. Zone 2 reveals peak before and after 3000 cm^{-1} which means there will be aryl, vinyl, as well as alkyl C-H. There is a peak at 2900 cm^{-1} and 2700 cm^{-1} which points to the presence of an aldehyde. There is no peak broad enough to be a carboxylic acid and there are also not enough oxygens for there to be one. Zone 3 reveals no peaks so there will be no alkynes or nitriles. Zone 4 reveals a significant peak at 1731 cm^{-1} . This corresponds to a carbonyl. This carbonyl can only be a ketone, ester, or aldehyde. It can't be a ketone because there is only one peak in Zone 4 and that has already been taken by the aldehyde. It can't be an ester because an

ester requires more than one oxygen. We see two peaks in Zone 5, around 1600 cm^{-1} and 1500 cm^{-1} . This points to the presence of a benzene ring. An alkene is not present because the benzene ring accounts for 4 DBE while the aldehyde accounts for 1 and there are not enough DBE for an alkene.

Step 5: Use NMR spectroscopy

The table in this problem has been given to us so all we have to do is fill in the blank spaces with the corresponding information. Let's start by filling in the hydrogen column which remember is given by the integral ratios. The total integral ratio is $1 + 5 + 1 + 2 + 4 + 6 = 19$. There are 19 hydrogens in our molecule so each unit of integral will yield 1 hydrogen. We can now plug in these values to complete the hydrogen column.

Shift	Splitting	Integral	#H	Implications
9.52 ppm	singlet	1	1	
7.40-7.27 ppm	multiplet	5	5	
4.71 ppm	triplet	1	1	
2.33 ppm	doublet	2	2	
1.58 ppm	quartet	4	4	
0.90 ppm	triplet	6	6	

The next step is to figure out the implications. The most obvious group is the benzene ring. Its splitting is often very complicated and multiplet and the chemical shift listed in the table is indicative of benzene. The fact that this group only has five hydrogens means that there must be a phenyl group that is replacing the missing hydrogen.

The next group that is fairly obvious is the first group. It has a singlet splitting pattern and has a chemical shift of 9.52. 9.52 is within the range of an aldehyde and the fact that we have an oxygen in our molecule as well as one hydrogen in this group is an indication that the group is an aldehyde.

The third group has one hydrogen and has two neighbors; the most obvious choice is a methine. The possible arrangements of this methine are being bonded to a methylene or being bonded to two other methines. The choice that creates the least number of atoms is the methine being bonded to a methylene so this is the most probable implication.

The fourth group has two hydrogens and one neighbor. It can be either a methylene or two methines. If it were a methylene, the only thing it can be bonded to would be a methine. If it were two methines, each methine would have to be bonded to another methine. The first possibility is more probable since it only involves 5 atoms instead of 8.

The fifth group has four hydrogens and 3 neighbors. It can be either 2 methylenes or 4 methines. If it were 2 methylenes, each methylene could be bonded to a methyl or it could be bonded to another methylene and a methine. If it is 4 methines, each methine could be bonded to a methyl, 3 other methines, or another methine and a methylene. The choice that creates the least number of atoms is when each of the two methylenes is bonded to another methyl group.

The last group has six hydrogens and two neighbors to couple with. It can either be two methyls, three methylenes, or six methines. If it were 2 methyls, then each methyl has to be bonded to a methylene. If it were 3 methylenes, each methylene could be bonded to another methylene or it could be bonded to 2 methines. If the group were 6 methines, then each methine could be bonded to two other methines or two a methylene. The choice that creates the smallest number of atoms is if the group were 2 methyls, each bonded to a methylene.

Shift	Splitting	Integral	#H	Implications
9.52 ppm	singlet	1	1	Aldehyde, O=CH
7.40-7.27 ppm	multiplet	5	5	Benzene ring with phenyl, C ₆ H ₅
4.71 ppm	triplet	1	1	CH in CHCH ₂
2.33 ppm	doublet	2	2	CH ₂ in CH ₂ CH
1.58 ppm	quartet	4	4	2 X CH ₂ in CH ₂ CH ₃
0.90 ppm	triplet	6	6	2 X CH ₃ in CH ₃ CH ₂

Now that we have all of our pieces, we need to check if we have any atoms unaccounted for. Adding up all the pieces yields: O + C + H + 6C + 5H + C + H + C + 2H + 2C + 4H + 2C + 6H = C₁₃H₁₉O. Our molecular formula that we derived from mass spectroscopy was C₁₄H₁₉BrO, so we are missing a carbon and bromine. The missing carbon must be a carbon with no hydrogens attached because it did not show up in the ¹H-NMR spectrum. We also have a bromine that is unaccounted for in the NMR spectrum.

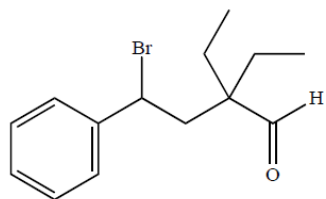
According to our DBE, we have five pi bonds to work with. The benzene ring takes up 4 and the aldehyde takes up the last one so we are left with no more DBE. All of our functional groups have been accounted from infrared spectroscopy and we can finally put the molecule together.

The two groups of CH₂ and CH₃ fit together and their splitting patterns agree with each other as long there are no other protons that can couple with them. We thus have 2 X CH₂CH₃. The CH and the CH₂ join together to give us CHCH₂ because these are the only two groups left that can fit together and their splitting patterns attest to this.

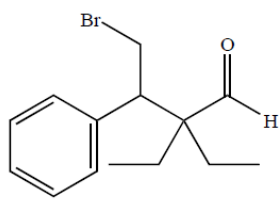
We now have a bromine atom, a carbon atom, a benzene ring, an aldehyde, 2 X CH₂CH₃, and a CHCH₂. The two CH₂CH₃ groups can only attach to the extra carbon because if they don't, their only other real option would be attaching to the CHCH₂ group. This would give the methine carbon four bonds which would prevent that group from bonding to the other pieces. Similarly, the only place to place the aldehyde and still be able to connect all the pieces is on this same group.

Therefore, we are now left with a bromine atom, benzene ring, a (O=C-H)C(CH₂CH₃)₂, and a CHCH₂. If we connect our (O=C-H)C(CH₂CH₃)₂ to the benzene ring, then there is no way for us to attach the other pieces as the central carbon of the group would have a full octet. The only way to connect all the pieces is to have the CHCH₂ between the benzene ring and the (O=C-H)C(CH₂CH₃)₂ group. The bromine must then be bonded to the CHCH₂ to complete the methine carbon's octet.

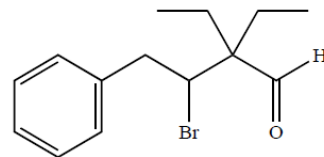
The possible structures from this are listed below:



Molecule A



Molecule B



Molecule C

Works Cited:

Dr. Hardinger's Lecture Supplement
Dr. Hardinger's Thinkbook
Illustrated Glossary from Chem 14C Website
Wikipedia for Molecular Structure Pictures