

Spectroscopy as Imagery¹

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Spectra measured by Ian Eck

Videos taken by Ian Eck and Clement Stormes

I was greatly inspired by the study of radiological studies (MRI, CT scans, bone scans and X-rays), which directed me to attempt a new approach to presenting spectroscopy. I think it will be valuable to focus on the topography or the landscape of the spectra, placing a little less emphasis on frequency and rules (though these are still important). The following is a treatment of each functional group and important visual features in IR, ¹H NMR and eventually, Mass Spectroscopy will be included.

“The spatial map of light that is a visual image does not have any intrinsic intellectual significance. The intellectual value of such an image primarily depends on the mental comparison of an image to the large library of images stored within the brain and the subsequent evaluation of the image’s meaning.”

“Most medical imaging is a process of pattern recognition, which basically involves comparing one image pattern with another. Evaluation for similarities and differences with known patterns results in a ‘best fit’ conclusion or ‘most likely’ diagnosis. This leads to the inescapable fact that a major factor in diagnostic efficiency is the observer’s development of a large image memory bank, which at least partially comes from viewing many images.”

Bushong, Stewart C. [Magnetic Resonance Imaging, Physical and Biological Principles](#) [give full reference](#)²

Success with this webbook is dependent on your studying the spectra that are available at http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng. Please view the Youtubes provided with this webbook, especially the Youtube that gives some guidance about how to access the spectra.

The linked website above is called the [Integrated Spectral Data Base](#). This is a very useful database and we use it continuously in the organic chemistry course. It is linked very prominently on our virtual reserves on the Bryn Mawr organic chemistry website which can be found at www.brynmawr.edu/Acads/Chem/mnerzsto/index.html. The more spectra you study of a particular functional group category, the better. You want to obtain a sense of the most prominent or distinguishing features of each functional group. Suggestions of specific compounds are given in each section, but you are encouraged to explore as many examples as you are able. The idea is similar to if you were taking an art class and your goal was to be able to identify a number of artists’ works quickly upon observation. How would you develop this skill? Clearly you

would not just read about it, you would at the very least need to study multiple examples of each artists work. So think of the spectral features of each different functional group as being like a particular artist work that contains his or her signature embedded in the style of the work. The spectra corresponding to a functional group class of alcohols, could be considered to be like a group of Degas paintings, the spectra for a family of carboxylic acids like a group of Van Gogh paintings, the aldehyde, like the work of Matisse, etc. Perhaps not as aesthetically pleasing to the nonchemist, but in some ways as complex and having their own unique signatures, though each spectrum of each individual compound will have its subtle differences even within a class. This part of the web book focuses on IR and ^1H NMR, but it will hopefully be extended to other forms of spectroscopy, such as Mass Spectroscopy. For the exercises described herein, please use the spectra on the data base for the "IR liquid film" if it is available and the highest megahertz (highest field) proton NMR spectrum possible in the database.

To assist you in your study of spectral landscape, there are spectra included for nearly every functional group that are covered in a normal organic chemistry course and these were measured at Bryn Mawr College. There are also Youtube videos that you can access that are referenced through the webbook to assist you in accessing the web data.

The first video deals with looking up IR and ^1H NMR spectra on the web and the topography or landscape of first few groups of functional groups, which are alkanes, cycloalkanes and haloalkanes.

Marc this youtube needs a name, like Spectroscopy as Imaging 1: Introduction and Introduction to Infrared Landscapes

Youtube: <http://www.youtube.com/watch?v=vSD2uSQzdr8>

The Second Youtube provides an introduction to proton NMR spectroscopy and some basic information about proton NMR "topography" or "landscape".

Marc, this youtube needs a name like Spectroscopy at Imaging 2: Introduction to NMR Landscapes.

<http://www.youtube.com/watch?v=is2yaKuZTxA>

Please note that if you visit the functional group worksheet on the organic chemistry website (www.brynmawr.edu/Acads/Chem/mnerzsto/index.html) it is linked to this page. When you visit this functional group worksheet on the organic chemistry website, just click on the functional group it will bring you to the section of this document relating to that functional group.

Please refer to the functional group overview found on the Bryn Mawr College Organic Chemistry web page at <http://www.brynmawr.edu/Acads/Chem/mnerzsto/FunctionalGroupOver.htm>

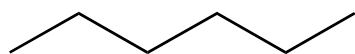
The Basic Infrared Spectral and Proton NMR Spectral Topography of Major Functional Groups

Alkanes and Cycloalkanes (Marc please link into appropriate portion of functional group worksheet)

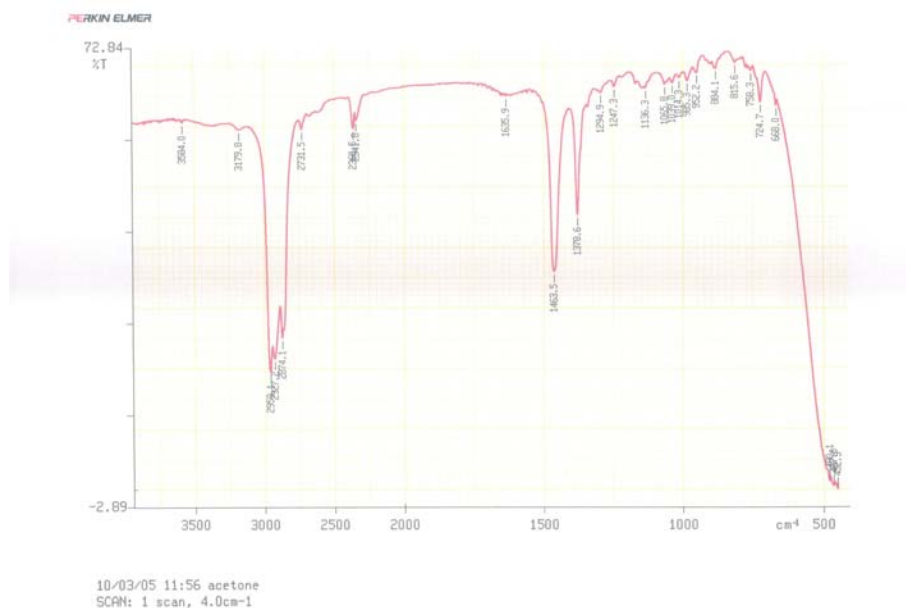
Infrared Spectra of Alkanes, Cycloalkanes

In this analysis we will be focusing on the functional group region of the IR, which is from about 4000 cm^{-1} (wavenumbers) to about 1500 cm^{-1} (wavenumbers). What would one expect in this region of the IR spectrum? One would really only expect to see the C-H stretching vibrational absorptions of the alkane or cycloalkane which would be found just below 3000 cm^{-1} (and for portions of molecules that are alkane-like in nature). It is generally centered around $2900\text{-}2800\text{ cm}^{-1}$. These absorptions are normally quite strong and sharp (extends to bottom of the page and are fairly narrow), though because organic molecules often have many different C-H groups, there can be several, overlapping spikes in this region. Find this region of absorption and note how similar it is from spectrum to spectrum. Organic compounds generally have sp^3 C-H stretching vibrations in this region. Why? You should expect to see these in nearly every spectrum irrespective of the functional group. Why? Look for these features in the given spectrum of hexanes given below and look up the IR spectrum of cyclohexane (structure shown below). To help out a bit, we have included some spectra from our laboratory, but remember you can visit the website as indicated in video at the beginning of this webbook.

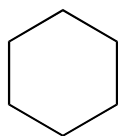
IR Spectrum of Mixed Hexanes



and other structural isomers



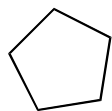
Please link up to the IR Spectrum of Cyclohexane using the database.



cyclohexane

Marc, Each one of these links has to have a name like Integrated Spectral Data Base
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng

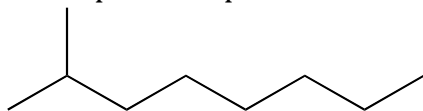
Look up the IR Spectrum of Cyclopentane



cyclopentane

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Look up the IR Spectrum of 2-methyloctane



2-methyloctane

2-methyloctane

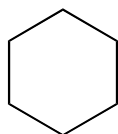
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Proton Nuclear Magnetic Spectroscopy of Alkanes and Cycloalkanes

Marc the above has to link into the appropriate place on the Functional Group Website.

In a similar manner to your web explorations involving IR, consider the proton NMR of cyclohexane, cyclopentane and 2-methyloctane.

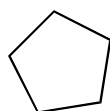
Please link into the proton nmr specrum of cyclohexane using the link below.



cyclohexane

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

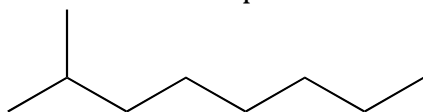
Please link to the proton nmr spectrum of cyclopentane using the link below.



cyclopentane

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Please link to the proton NMR of 2-methyloctane on link below.



2-methyloctane

2-methyloctane

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

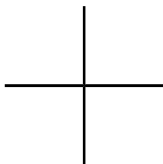
When you study the landscape of the referenced proton NMR spectra what becomes evident? You should notice that each spectrum only shows one peak or several peaks from approximately .9 – 1.4 ppm (part per million are the units of NMR and are proportional to frequency as wavenumber is in IR).

Though this treatment of NMR is not truly delving into theory, the position of NMR peaks is related to the net magnetic field the protons in question experience from the local fields produced by electrons circulating in their environment. These local fields are influenced by local electronegative atoms as well as the circulation of electrons in pi bonds, among other factors. What is important to note here is that a

“run of the mill” or typical hydrogen in an alkane or cycloalkane has peaks around 1 ppm (around means a little below or a little above). These are sp^3 hydrogens and in a proton nmr you are only observing the protons and how they are effected by surrounding atoms. There are really no structural elements in these particular compounds to significantly alter the magnetic field, so the hydrogens are all at or around 1 ppm. You will also notice that for the first two compounds, only one proton peak is observed. For 2-methyloctane, it should appear to be more complicated. In these spectra and in all proton spectra, you are observing how the symmetry of structure effects the NMR. You will observe one peak for each type of hydrogen you have in the structure. In cyclohexane and cylcopentane, all the hydrogens are the same by symmetry so they all experience the same net magnetic field and all absorb at the same low frequency. Therefore, only one peak is observed. In other alkanes, the spectra are more complicated, though the peaks observed are all slustered around 1 ppm. The he hydrogens are not necessarily the same so there can be multiple peaks overlapping as shown below with the example, 2-methyloctane. Notice there is more than one peak, but all are around 1 ppm. Think about the structure of 2-methyloctane? How many peaks would you predict based on the number of different types of hydrogens? The reason they are close together in the spectrum is because the environments are not sufficiently distinct from a magnetic perspective.

As another exercise, examine the spectrum of tetramethylmethane, obtainable on the website linked below. Please continue to study other alkanes and cycloalkanes so that they become completely recognizable to you.

Please link up to the spectrum of Tetramethylmethane on the website link below.



tetramethylmethane

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

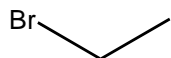
Infrared Spectra of Haloalkanes

Marc Link the above to the appropriate place on my functional group worksheet. Link to haloalkane

The IR of haloalkanes in the functional group region (the region between about 4000 and 1500 cm^{-1}) is very similar to that of alkanes because the absorptions of halogen groups are in the fingerprint region (well below 1500 cm^{-1}) of the spectrum.

Note: the only significant absorption in the functional group region of the IR spectrum is just below 3000 cm^{-1} . This is the CH stretching vibration of the sp^3 C-H groups yet again. Does it make sense that a molecule with a function group can have portions that are alkane-like in nature? This is true of most organic compounds. You expect to see alkane features in most IR and NMR spectra. There are absorptions from the C-X bond in the finger print region at 600-800 cm^{-1} . Please examine the spectra of 1-bromobutane provided below and study at least the spectra on the spectral database for these IR features.

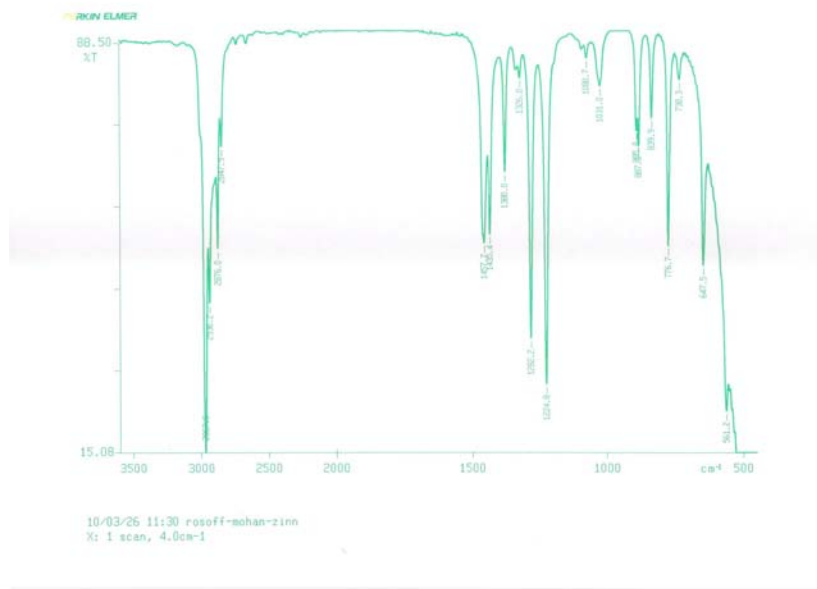
Please link to the infrared spectrum of ethane on the website link shown below.



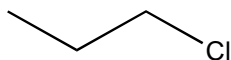
bromoethane

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Please study the infrared spectrum of 1-bromobutane provided below.



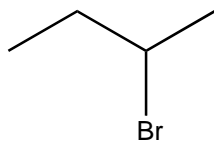
Please link into the IR spectrum of 1- chloropropane at the website link provided below.



1-chloropropane

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Please link to the IR spectrum of 2-bromopropane using the website provided below.



http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

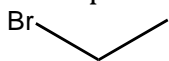
Proton NMR of Haloalkanes

Marc, this should be linked to the appropriate location of the functional group worksheet.

In the proton NMR of a haloalkane, all you should expect is a higher position in ppm for the hydrogens two bonds from the halogen (the halogen significantly perturbs the magnetic field of the hydrogens that are close by, raising it and thus, a higher frequency is needed to excite the protons). Usually hydrogens near the halogen are in the 3-4 ppm range. One expects more typical hydrocarbon positions (like alkanes and cycloalkanes) for the other hydrogens in a haloalkane. At this point, you should be starting to observe spectral splitting patterns. When hydrogens are adjacent (three or fewer bonds away) from hydrogens that are in a different environment, you will observe splitting (the peaks will not be single peaks, but rather have a pattern that communicates the number of adjacent, but different (magnetically distinct) hydrogens). At this point we are going to focus on a couple of alkyl patterns that would be useful for you to learn to recognize in this early phase of our studies. In your study of the proton NMR imagery below of the compounds bromoethane, 1-chloropropane and 2-bromopropane you will see the patterns for an ethyl group (a triplet and quartet), a propyl group (a triplet, a multiplet and a quartet) and an isopropyl group (a large doublet and a multiplet), respectively. A doublet appears as two peaks that are in very close proximity and are close to each other in size. A triplet is a group of three peaks that appears in close proximity (the distances between the peaks are equal and are in a 1:2:1 area ratio – this is apparent in the heights. A quartet is a group of four peaks that is in close proximity, has distances that are the same between the peaks and have a ratio of 1:2:2:1. One observes one more peak than the number of different (magnetically distinct) proton neighbors (protons on adjacent carbons (normally)). This is a just a beginning, but study of the spectra should help you to become visually oriented.

Study the proton NMR spectra of the following suggested compounds (and as many as you can on the website). What are the positions of the peaks in each spectrum? What do the splitting patterns tell you about numbers of neighbors? Are these spectra what you would expect for the structure of the given haloalkane? Try to find the patterns alluded to above. Can you find them and name them? Can you interpret them.

Link up to the proton NMR spectrum of bromoethane at the website link below.

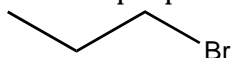


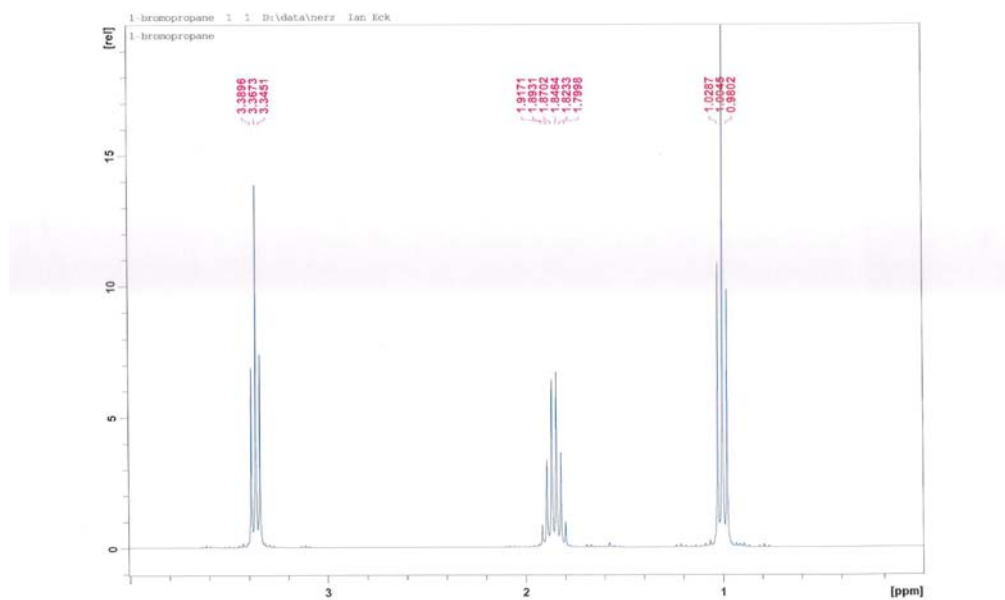
bromoethane

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Please study the proton NMR Spectrum of 1-bromopropane shown below.

1-bromopropane:





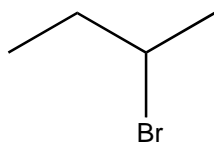
Link up to the proton NMR Spectrum of 1-chloropropane using the website link given below.



1-chloropropane

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Link up to the proton NMR Spectrum of 2-bromopropane shown below.



2-bromobutane

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

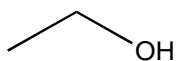
Infrared Spectroscopy of Alcohols

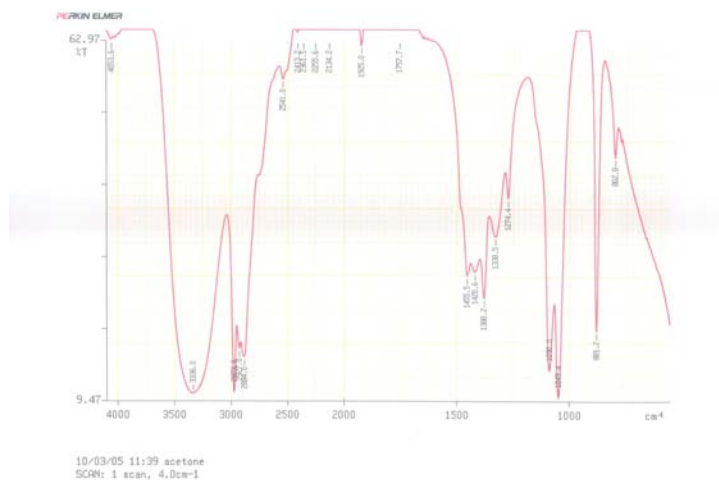
Marc, this should be linked to the same group on the functional group worksheet.

What do we expect for alcohols (OH groups) in infrared spectroscopy? The alcohol functional group shows up very prominently in the functional group region of the infrared spectrum. The OH stretching vibration normally appears as a broad and strong absorption at about 3300 cm^{-1} . What this means is that it has a high intensity and the peak has a large width. The reason for this is due to various hydrogen bonded states that the molecules exist in when at high concentration or “neat” (pure liquid). Frequently, IR spectra are measured as a “neat” liquid. Why would you expect alcohols to hydrogen bond when in a pure or relatively concentrated state? If the OH group is not hydrogen bonded, as in a solution diluted with a non-hydrogen bonded solvent, the OH would be at a much higher position (3600 cm^{-1}). The OH functional group is topologically very distinct. In simple alcohols we would only expect to see the C-H sp^3 stretching vibration due to the alkane part of the molecule just below 3000 cm^{-1} in addition to the broad peak at 3300 cm^{-1} . Please note these two features in the following suggested alcohols (and any others you choose to research). Please focus on the topography or landscape of the functional group region. Focus on the similarities in the functional group regions and not the differences in the finger print regions. You want to be able to look at an IR and immediately recognize the functional group. Alcohols should jump out at you because of their unique landscape. Link to the following alcohols on the sited spectral data base. Find the features outlined above. It is also a good idea to meticulously study each structure and consider the IR features it should produce.

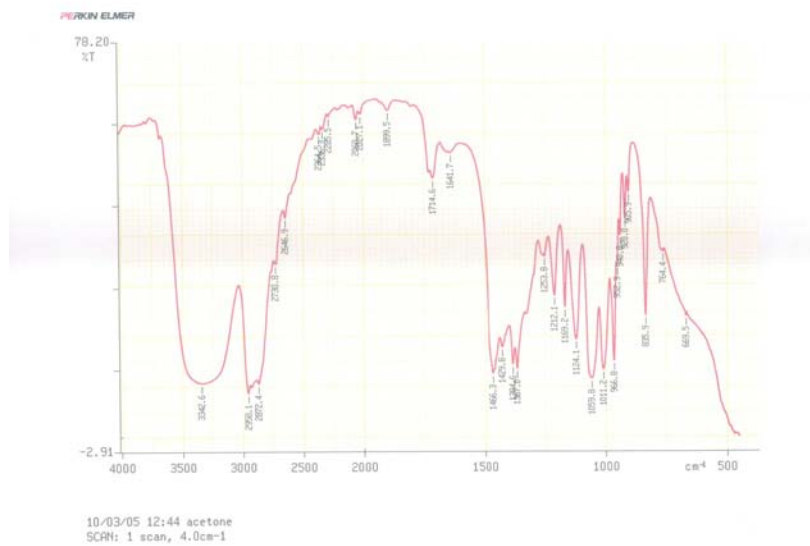
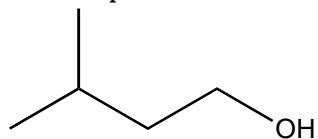
The spectrum of ethanol is included here for your convenience. Start with it and then go to the website to look up more spectra. Don't feel restricted to the alcohols given, you can look up as many spectra as you wish. It is to your advantage to do so.

The IR Spectrum of Ethanol is provided below.

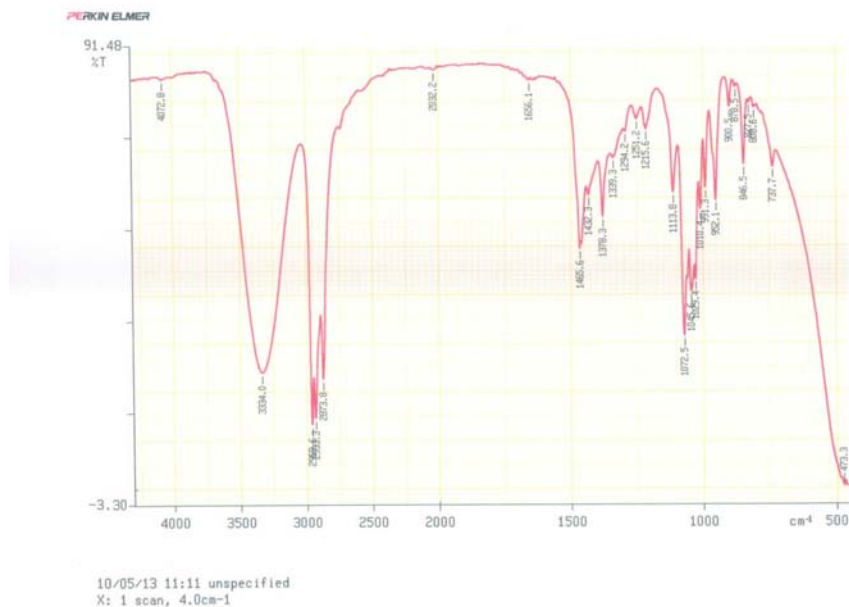
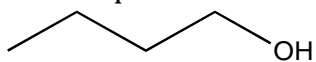




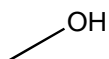
The IR spectrum of isoamyl alcohol is provided below



The IR spectrum of 1-Butanol is Provided Below



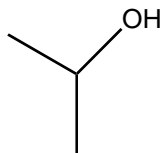
Please link up to the IR Spectrum of methanol using the website link below below.



methanol

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Link up to the IR Spectrum of 2-propanol using the website link given below.



2-propanol

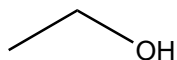
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Proton NMR Spectroscopy of Alcohols

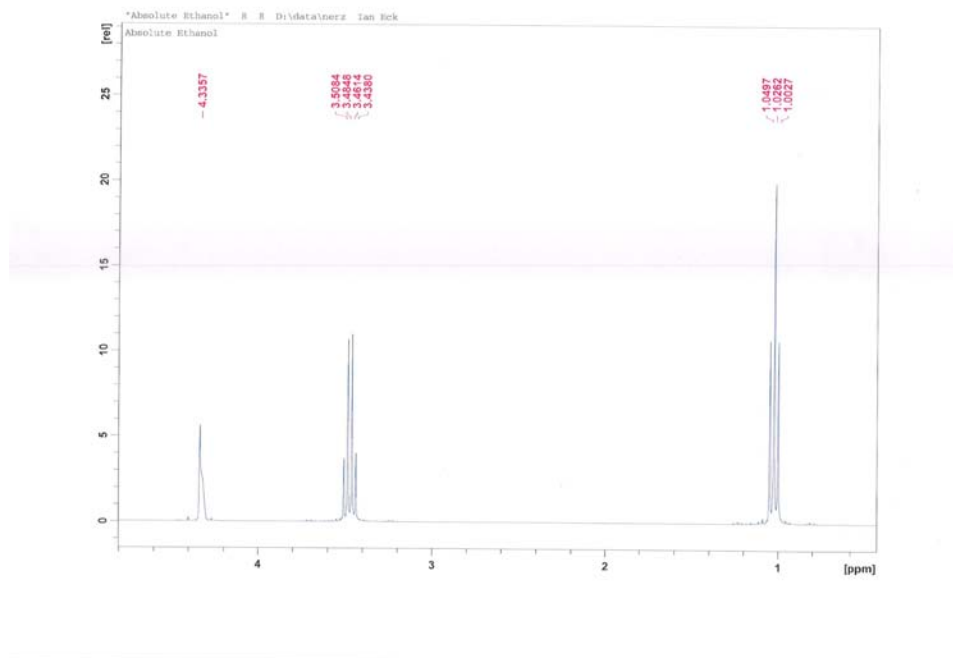
Marc, this should be linked to the functional group worksheet at the place where it says alcohols.

In ^1H NMR one expects the alcohol to have three major features. 1. In typical spectra which are run in slightly acid contaminated solvent, one expects a single peak for the hydrogen on the oxygen. 2. One expects the hydrogens on the carbon closest to the oxygen to be at a higher position, i.e., 3-4 ppm (rather like being near a halogen). 3. One expects the rest of the molecule to behave like an alkane or cycloalkane in that there will be peaks around 1 ppm. 4. The hydrogen on the alcohol can be anywhere from 0.5 to 5 ppm depending on the extent of hydrogen bonding. 5. The way proton NMRs are typically run, the OH peak will probably not exhibit the splitting properties described regarding alkyl chains. It is a position difficult to predict and should not be relied upon for identification. The proton NMR spectrum of ethanol is included here for your convenience. Can you find the OH peak? Remember it will be a singlet in all likelihood, but in an unpredictable position. Find the CH_2 hydrogens next to the oxygen. They should look like a quartet and be at about 3-4 ppm. The methyl hydrogens should be at the position of a normal alkane. Are they? What is their splitting pattern. Did this chain give the splitting pattern you expected.

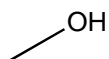
Please study the proton NMR Spectrum of 1-Ethanol provided Below



1-ethanol



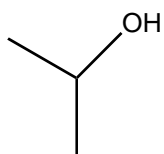
Link up with the proton NMR spectrum of methanol using the website link given below.



methanol

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

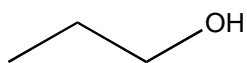
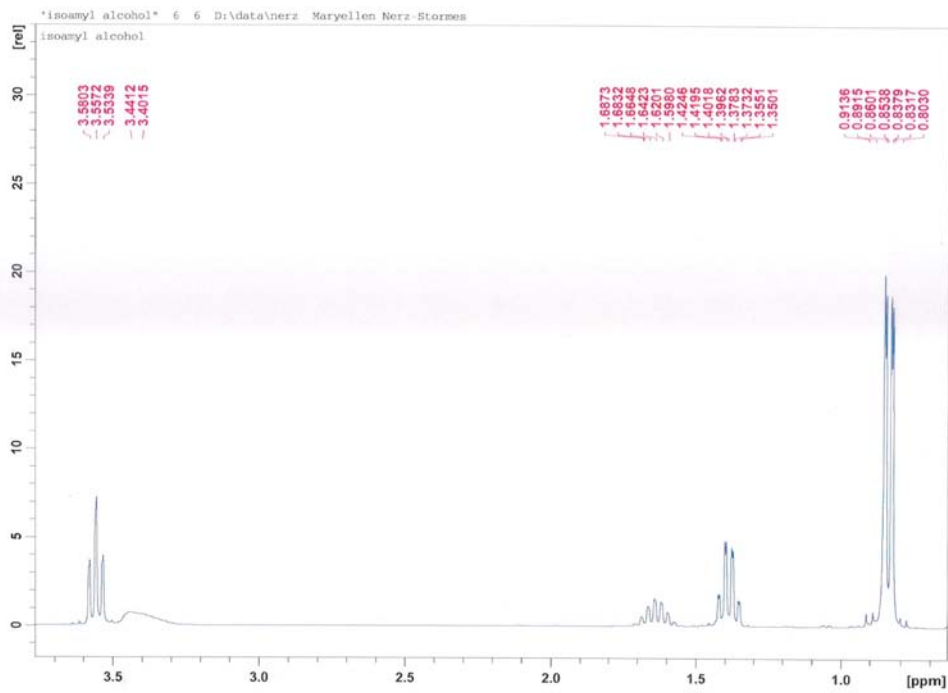
Link up with the proton NMR spectrum of 2-propanol on the website link given below.



2-propanol

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

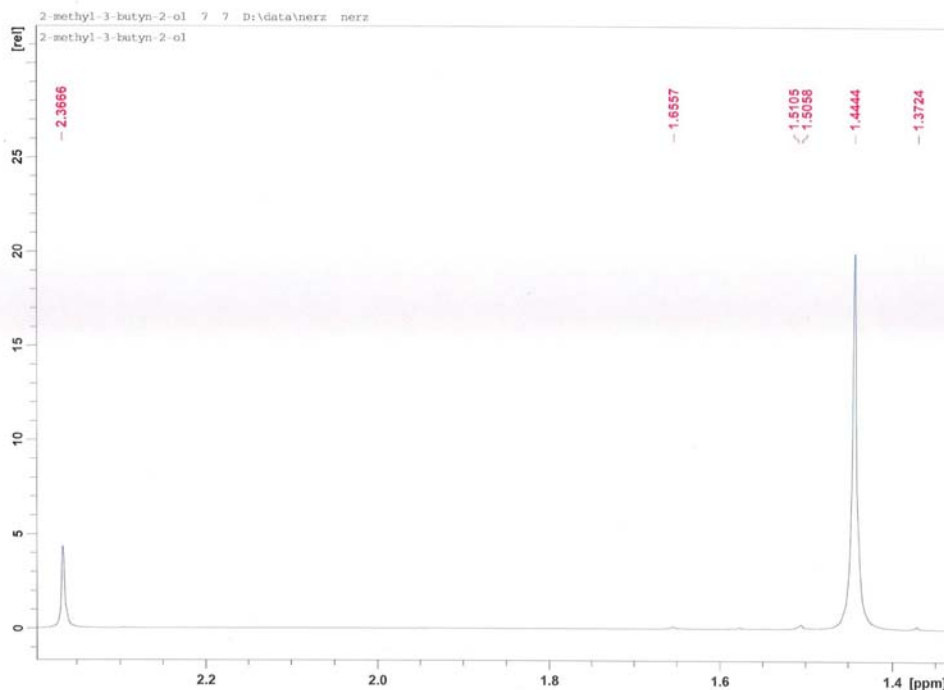
Study the proton spectrum of 1-butanol provided below.



1-butanol

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

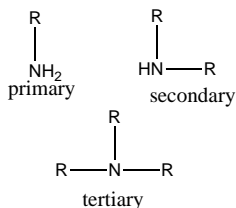
Please study the proton NMR Spectrum of 3-methyl-butyn-1-ol that is provided below.



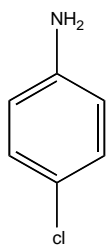
Infrared spectra of Amines

Marc please link this into my functional group worksheet at amines.

Amines can be primary, secondary or tertiary as shown below. The most characteristic aspect of the IR spectrum is there are two peaks for a primary amine at around 3500 cm^{-1} and 3400 cm^{-1} and a single peak for a secondary amine in this range. There is no peak observed for a tertiary amine. The peaks for the primary and secondary amines are due to the N-H stretching vibrations. Of course, a tertiary amine does not have any N-H bond. Other than that, an amine should really only show C-H stretching vibrations around 3000 cm^{-1} .

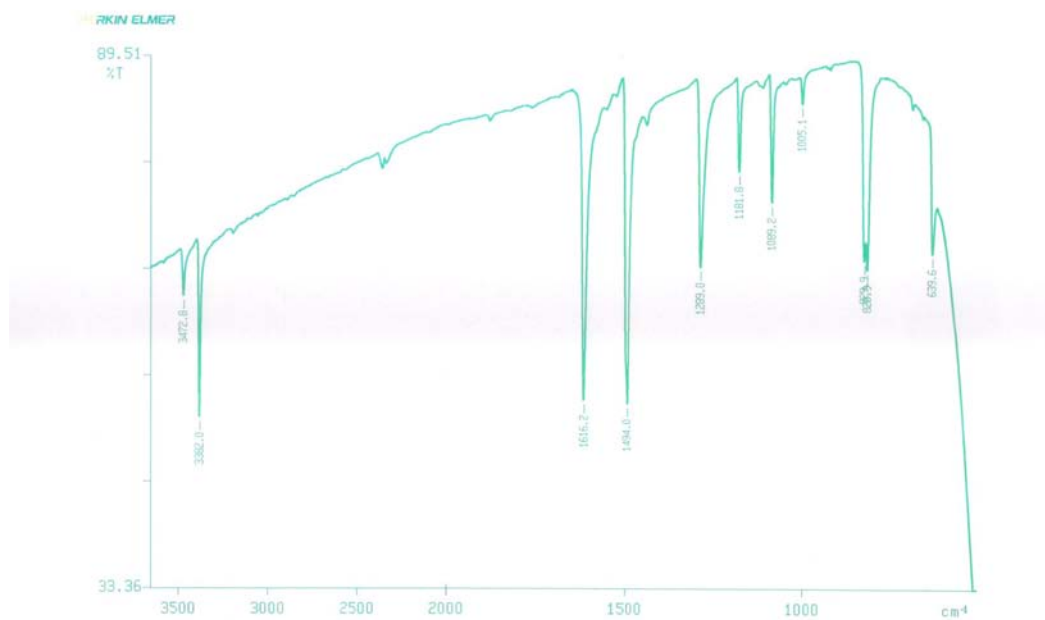


The IR Spectrum of 4-chloroaniline (also an aromatic and halogen compound) is provided below.



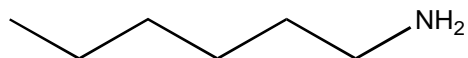
p-chloroaniline

Note: the following spectrum is a solid state spectrum run as a solid film and the C-H stretching vibration region is very weak. This means the spectrum was run as a solid, where most of the spectra included in this webbook are run as liquid films. Solid state spectrum when not run optimally can have a slant to the baseline (as you are seeing) and weak absorption in the low frequency part of the spectrum. The two prominent peaks above 3000 cm⁻¹ are due to the N-H stretching vibrations of the NH₂.



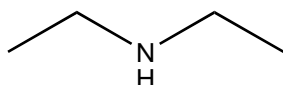
10/04/15 13:54 Peter hexaPhBenzene
X: 1 scan, 4.0cm⁻¹

Link up with the Infrared spectrum of hexylamine using the link below.



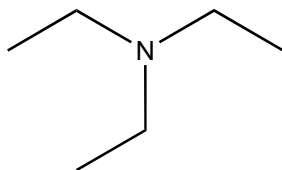
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Link up with the infrared spectrum of N, N-dipropylamine using the link to the integrated spectral data base shown below.



http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Link up with the infrared spectrum of triethylamine using the link to the integrated spectral data base provided below.



http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Please study these spectra and note the prominent features in the functional group part of each spectrum.

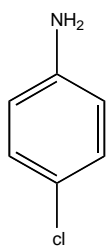
Proton NMR of Amines

Marc this should be linked to the section titled amines in my functional group worksheet.

The proton NMR of amines has similar features to the NMR of an alcohol.

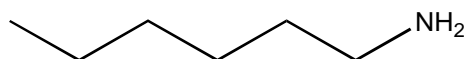
1. The hydrogen on the nitrogen is usually a singlet and can be in variable location, sometimes it appears as a broad singlet. 2. The hydrogens on the carbon or carbons next to the nitrogen will be at a significantly increased position relative to the normal hydrocarbon hydrogens. 3. One would expect the normal features of a hydrocarbon for the rest of the structure, provided there are no other functional groups.

The proton nmr spectrum of 4-chloroaniline (also an aromatic and halogen compound) is provided below. Where is this spectrum?



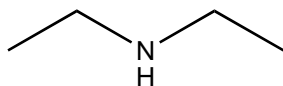
p-chloroaniline

Link up with the proton nmr spectrum of hexylamine using the link below that will connect you with the integrated spectral data base.



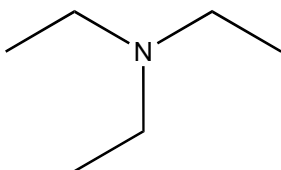
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Link up with the proton nmr spectrum of N, N-dipropyl amine using the link provided below that will connect .



http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Link up with the proton nmr spectrum of triethylamine.

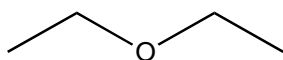


http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

The Infrared Spectrum of Ethers

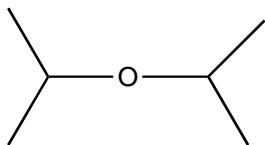
Infrared spectrum of ethers has some common features with that of alkyl halides in that the spectrum only has features of a hydrocarbon in the fingerprint region of the spectrum. Therefore, one would only expect to see the sp^3 C-H stretching of an alkane just below 3000 cm^{-1} , provided there are no other functional groups. The C-O stretching vibration of the ether functional group appears at around 1100 cm^{-1} , which is in the fingerprint region of the spectrum. Therefore, expect a simple ether to look like an alkane.

Link up with the IR spectrum of diethyl ether.



http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Link up with the IR spectrum of diisopropyl ether



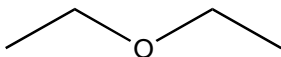
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Please draw the structure of various ethers (create your own) and locate their spectra on the referenced or other website and once again observe and study their features. Please look up many spectra. The more you do this the better you will be at interpreting spectra when you learn the theory.

The Proton NMR of Ethers

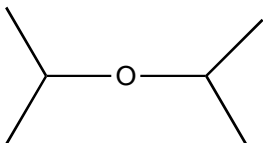
The proton NMR of ethers has similar topographical or landscape features to the proton NMR spectra of haloalkanes. One would expect the normal features of an alkane, including splitting, most peaks being in the range of ca. 0.9-1.5 ppm. Like haloalkanes, you would expect the hydrogens on the carbons directly attached to the oxygen to appear in the region 3-4 ppm.

Link up with the proton NMR spectrum of diethyl ether.



http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Link up with the proton NMR spectrum of diisopropyl ether.



http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Please take notice of the splitting patterns in the above two compounds. In the first, diethyl ether, you should observe a triplet and a quartet. The quartet indicates that the absorbing hydrogens are adjacent to three magnetically distinct hydrogens, i.e., a methyl group. The triplet indicates that the observed hydrogens are adjacent to two magnetically distinct hydrogens. Notice only two groups are observed because diethyl ether is symmetrical. The NMR can't distinguish hydrogens that are the same. They absorb at the same radiofrequency. In the second, you should observe the distinctive pattern of isopropyl groups. Isopropyl groups should have a small heptet and a large doublet. You might want to note at this time that the area under the group of peaks is proportional to the number of hydrogens absorbing. This is the reason for the relative sizes of the peaks.

Alkenes

Infrared Spectrum

The functional group region of an alkene has a very distinctive, but consistent appearance. There are of course, sp^3 C—H absorptions because most alkenes (all except ethene) have sp^3 C-H absorptions. By now you should know where this type of bond absorbs in the functional group region. You would expect most alkenes to have an alkane component and therefore, you should observe peaks just below 3000 cm^{-1} . You would also expect a typical alkene to have sp^2 C-H absorption or absorptions just above 3000 cm^{-1} . This is because most alkenes do have sp^2 C-H bonds. One alkene that would not have the sp^2 C-H stretch would be 2, 3-dimethyl-2-heptene. You can look it up at our favorite website at http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi.

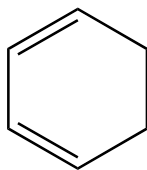
Therefore, in terms of landscape, one expects to see two clusters of absorptions around 3000 cm^{-1} in the typical alkene spectrum. One group of absorptions just above 3000 cm^{-1} and one just below. Additionally, in the functional group region, one expects a C=C stretching absorption. This would be at about $1600\text{--}1660\text{ cm}^{-1}$ in the typical molecule. Note: there are C-C stretching absorptions for most organic

molecules, but these are in the fingerprint region. It is noteworthy and will be explained in other materials, that alkenes with symmetrical double bonds do not absorb in the region around 1660 cm^{-1}

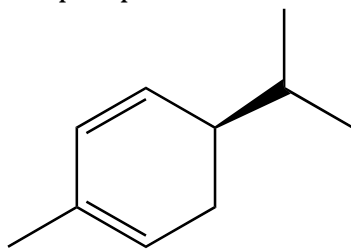
Summing up, there would be absorptions just above 3000 cm^{-1} , just below 3000 cm^{-1} and an absorption at or around 1640 cm^{-1} . Note: not all alkenes give C=C stretching absorptions – symmetrical bonds do not absorb in the infrared. Generally, the sp^2 C-H absorptions just above 3000 cm^{-1} are fairly strong and sharp as described earlier for alkanes. The alkene peak tends to be weak or nonexistent depending on the polarity of the bond. See if you can observe this trend in the study of spectra of alkenes.

The spectra of 1,3-cyclohexadiene and alpha-phellandrene are given below for your convenience. Go over the two structures and make a list of what you would expect to see for these compounds and then study the following spectra, looking for the predicted features based on the information discussed above.

1,3-cyclohexadiene



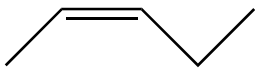
R-alpha-phellandrene



Where are these spectra???

Consider the following compounds on the Integrated Spectral Data Base in the range from 4000 cm^{-1} to 1500 cm^{-1} . This is, just to remind you, of the range of the functional groups found in most organic compounds.

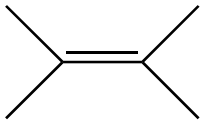
Link to the spectrum of cis-2-pentene.



cis-2-pentene

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Link to the spectrum of 2,3-dimethylbutene



2,3-dimethylbutene

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Link to the spectrum of cis-2-heptene



cis-2-heptene

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Did you observe the general patterns of absorptions in the spectrum described in the previous text? If you did not, can you explain why? It is helpful to carefully look at the wavenumbers given with the spectra to examine the positions of peaks, but a good eye can normally tell if a peak is above 3000 cm^{-1} or below 3000 cm^{-1} . Feel free to peruse other alkenes in the data base. Use your knowledge to come up with other compounds to study. It is a good idea to study as many spectra as possible to start to recognize the IR patterns of basic functional groups in organic chemistry.

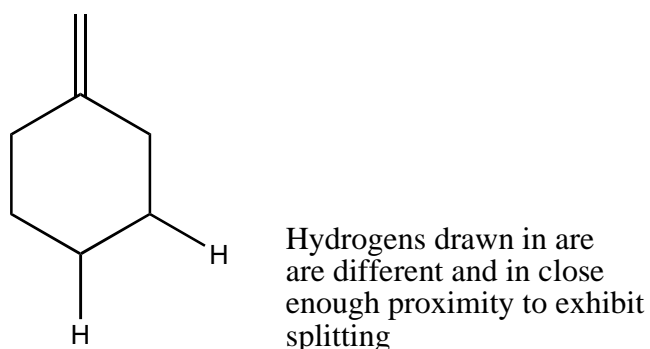
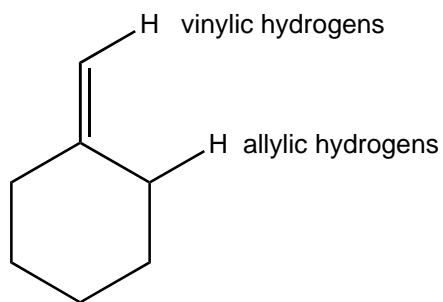
Proton NMR of Alkenes

Based on the patterns you have observed and what you have learned about the topography of spectra, what general characteristics would you expect to find in the proton spectrum of an alkene?

Please note again, that the only components of the molecule observed in a proton spectrum are the hydrogens. The hydrogens on the double bond are at special locations in the NMR spectrum. One expects to observe them in the approximate region ranging from 4.5-5 ppm. There will be peaks for the protons on the carbon nearest the double bond (called the allylic position) in the approximate range of 2-2.5 ppm and the rest of the hydrogens should be in the region where normal relatively unperturbed hydrogens are normally be found. Where is this? Yes, in approximately the range from .8-1.5 ppm. There can be single peaks or split peaks

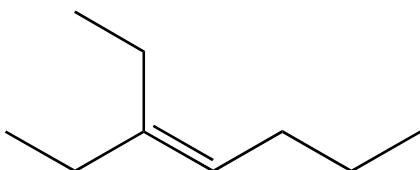
depending on the structure of the compound as described earlier. Normally, hydrogens that are different, but near each other in the structure (this would be three or fewer bonds away normally) exhibit a phenomenon termed splitting such that the peaks appear as groups of peaks, rather than individual single peaks. Hydrogens that are the same and are far from other hydrogens in the molecule

appear as single peaks. Note they can be near heteroatoms but not near hydrogens on carbons.



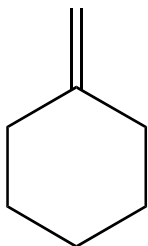
Consider the following molecules from an nmr perspective. Look them up on the integrated spectral data base.

2-ethyl-3-heptene, methylene cyclohexane



2-ethyl-3-heptene

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi



methylenecyclohexane

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Draw a structure of vinylic and allylic hydrogens.

What is it about the spectrum that makes you suspect it is an alkene? Can you find the vinylic hydrogens in the range from 4.5-5 ppm? Can you find the allylic hydrogens? Where are the normal, alkane like hydrogens. Why, in the first compound do you observe a triplet and quartet (one of the normal alkyl patterns given above). Why are the non allylic and allylic hydrogens hard to distinguish in the proton nmr of the second compound?

You are encouraged to look at other alkenes. Please do. Draw structures, name the compounds and look them up on the data base.

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Alkynes

Infrared Spectra

Alkynes are like alkenes in that one expects to observe the stretching vibration of the C-H bonds on the triple bond in a unique position and to hopefully see the triple bond itself. The rest of the molecule should really look like a typical alkane. The C-H bond of an alkyne (If it has one – many alkynes do not, why?) is found at approximately 3300 cm^{-1} in the infrared spectrum. One might wonder how this peak might be distinguished from the OH of an alcohol given they absorb at similar frequencies, but it is quite distinguishable because rather than exhibiting the broad strong peak of an alcohol, it exhibits a very sharp strong peak as exhibited in the spectra noted below.. This terminology means that when you observe the peak, it will appear to be very intense (close to the bottom of the image), but relatively narrow across.

The only alkynes that exhibit a sp C-H absorption are those that have terminal alkynes, that is, alkynes that are at the end of a chain. Internal alkynes show no sp C-H absorption because they have no C-H bond. As indicated in the prior text, this

absorption is a sp C-H stretching absorption and it occurs in a distinct frequency range from from sp² C-H and sp³ C-H.

Why am I calling this a sp CH? Review hybridization from lecture. Once again, reviewing the three hybridizations – sp CH is at or around 3300 cm⁻¹, sp², in a range just above 3000 cm⁻¹ and sp³ CH just below 3000 cm⁻¹.

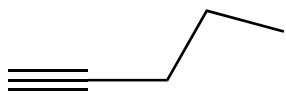
Sometimes observed is the triple bond itself which normally absorbs in the region around 2200 cm⁻¹. It is very often a weak or nonexistent absorption. This is because the strength of an absorption in an IR depends on two factors, the polarity of the bond and the number of the bonds. Frequently C-C bonds will not be very polar and sometimes there will be no polarity.

Go over the functional group regions of the following compounds. Once again, the functional group region extends from 4000 cm⁻¹ to about 1500 cm⁻¹. Also, it is incredibly important in this exercise that you look the spectra up on this or another internet site. Not only will you really become more comfortable and facile with spectra, but you will really learn the major organic functional groups. This is extremely important in organic chemistry.

Link up to the infrared spectra of the following compounds.

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

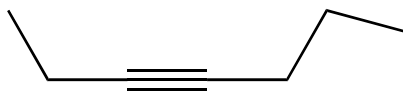
1-pentyne, 2-hexyne, 3-heptyne



1-pentyne



2-hexyne



3-heptyne

What major absorptions do you observe in the functional group region of 1-pentyne. Are you able to distinctly identify the sp^3 and sp stretching vibrations in the functional group region? Can you find the triple bond stretching vibration in the functional group region? What is different about the infrared spectrum of 2-hexyne in the functional group region?

Why is the infrared spectrum of 3-heptyne unique? Why is there no triple bond absorption showing up in the infrared spectrum of three heptyne?

Proton NMR of Alkynes

The 1H (proton) NMR of course of any compound can be greatly complicated by the splitting of nearby hydrogens. Remember, you are only seeing the hydrogens in proton or 1H NMR, but there are fundamental things to look for when first observing and studying the topography or landscape of a proton spectrum of an alkyne.

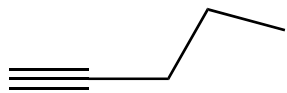
First, due unique positioning in the magnetic fields of the NMR spectrometer and induced within the molecule by the magnet of the NMR spectrometer, the hydrogen on the triple bond (only in terminal alkynes!) is normally in the range from 1.8-2 ppm and is frequently at a lower ppm position than the hydrogens on the carbon next to the functional group. Similar to alkenes, these are in the range from 2-2.5 ppm. They will show splitting or not depending on the proximity to different neighbors. The rest of the hydrogens in the molecule will behave as normal alkyl type hydrogens, splitting when close to different neighbors and being observed in and around 0.8 -1.5 ppm as described earlier.

To get a good sense of the topography or landscape of alkynes in proton NMR, you should focus on the same compounds as you did for IR. i.e., 1-hexyne, 2-hexyne and 3-heptyne, though you are welcome to study others as well! While doing this think about the number of peaks you should see for each compound. Where should you see splitting. Are any peaks or groups of peaks that are overlapping. This is a common feature of nmr. Peaks frequently overlap.

Please consider the following proton nmr of

Link up with the proton NMR spectra of 1-hexyne, 2-hexyne and 3-heptyne.

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi



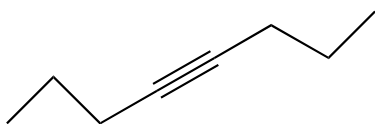
1-pentyne



2-hexyne



3-heptyne



3-octyne

Once again, it is not bad to work through the compound and the types of hydrogens present to predict what the NMR would be like. It is a good structural exercise even for the novice student. Are you able to find the hydrogens that are on the carbon next to the triple bond. These should occupy the highest ppm position in the spectrum. The hydrogen on the triple bond (once again, only if terminal) would come next. Then the rest of the chain should look like a normal alkyl chain. Notice that the triple bond itself never shows up as it is comprised of carbon and the compound, 3-octyne nicely demonstrates the effect of symmetry in NMR. Only different hydrogens show up in an NMR. So as far as the NMR spectrometer is concerned, it basically sees three types of hydrogens so only three groups of peaks will be observed in the proton NMR of 3-octyne. It can't distinguish hydrogens that are identical. Also, this compound demonstrates the propyl group that was described earlier, i.e., it shows up as a triplet, multiplet, triplet combination.

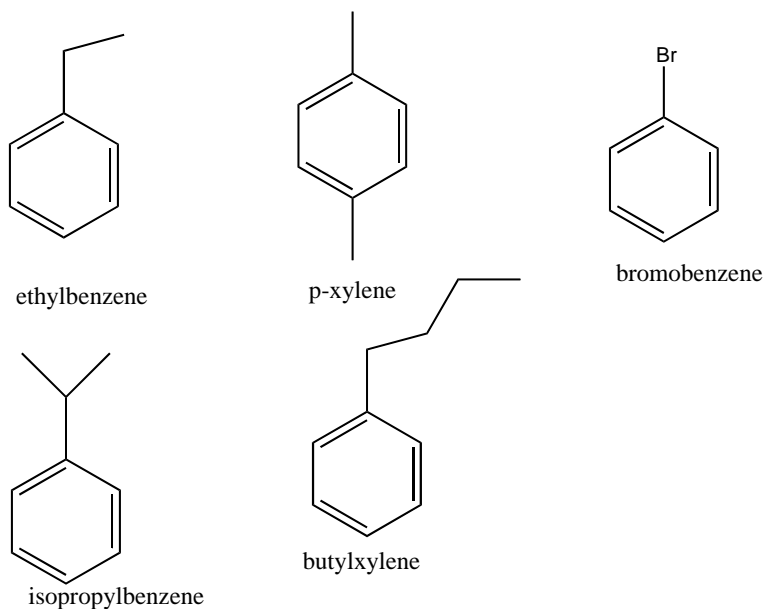
Aromatic Compounds

Infrared Spectroscopy of Aromatic Compounds

In the functional group region of the infrared spectrum, one expects certain fundamental features of an aromatic compound and for your purposes at this point this would normally be benzene or compounds containing a benzene ring or benzene rings. First, one expects sp^2 C-H stretching (why – knowing this very much relies on you knowing structure- what hybridization would you predict for a carbon in a benzene ring). Based on your study of alkene infrared spectra, where would this be? Just like an alkene or at least similar to an alkene, there should be sp^2 C-H stretching absorptions in the region just above 3000cm^{-1} . Actually, they are normally at approximately 3050cm^{-1} , but recognizing they should be above 3000cm^{-1} is adequate at this point. I hope you are starting to use 3000cm^{-1} as a boundary to determine which kind of hydrogens you have on the carbons in your molecule (and to determine the hybridization of carbons). If the aromatic also contains a hydrocarbon chain of some sort, one would expect C-H stretching absorptions at just below 3000cm^{-1} . The aromatic ring itself shows stretching absorptions at or around 1600cm^{-1} and 1500cm^{-1} . It has some similarities to an alkene, but it is not truly an alkene – why? Very frequently chemists will identify an aromatic compound by the observation by a characteristic series of absorptions normally found in the range from $2000\text{-}1600\text{cm}^{-1}$. These are very low and somewhat regular; about 4 or five low bumps in the baseline. At this point, you should not put too much emphasis in low absorptions in the baseline in your landscape evaluations, but these are noteworthy. These are called aromatic overtones and are absorptions that occur at multiples of other absorptions. They will be discussed a bit more in class.

To observe the features described in the text above, please study the spectra of the following compounds by linking to the cited website.

Ethylbenzene, isopropylbenzene, p-xylene, butylbenzene, bromobenzene



http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Study of the functional group region of the IR (again focus on what is the same, not what is different) should yield very similar looking spectra for all the compounds, except one. For alkyl benzenes, one should see absorptions above 3000 cm^{-1} due to the sp^2 C-H bonds and just below 3000 cm^{-1} for the sp^3 C-H bonds. One should also observe moderate peaks in the range 1600 and 1500 cm^{-1} from the stretching of the C-C bonds in the aromatic ring itself. Can you find the aromatic overtones described earlier? Verbalize or write out which bonds are giving rise to each absorption. By now, it should be clearer that IR spectroscopy gives you information about bonds and NMR information about atoms (different atoms depending on the type of NMR, proton NMR gives you information about hydrogens in the structure).

Once again we do not expect incredibly strong absorptions for the bonds of the aromatic ring, i.e., the carbon-carbon bonds because they are not very polar in most cases. What is different about the bromo aromatic? For this compound, you should only see sp^2 C-H stretching vibrations and the absorptions due to the C-C bonds of the aromatic ring. The C-Br bond absorbs deep into the fingerprint region (at very low wavenumber, frequency).

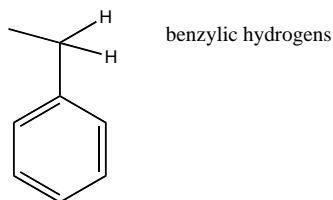
Proton NMR of Aromatics

The proton NMR of aromatic compounds is very interesting. The protons on an aromatic ring have unique positions in the NMR spectrum, usually absorbing in the range from 6-8 ppm. This is a very high frequency or high ppm position for hydrogens that are merely bonded to carbon. Normally, hydrogens bonded to carbon are found in the range from 0.8-1.5 ppm, but the pi bonds in molecules, particularly those in aromatic compounds circulate in the magnetic field produced

by the spectrometer, inducing magnetic fields which greatly distinguish protons in close proximity to these fields. This unique position results from what is called a ring current effect and is taken as experimental evidence that the molecule being studied contains an aromatic ring or rings. As the course continues, you will have stronger theory to back up these observations. At this point, they are simply observations. Therefore, if you see a peak or peaks in this range you should assume you have an aromatic compound, which is most likely a benzene ring. Most of the time, at this level, a peak or peaks between 6-8 ppm indicates the presence of a benzene ring in the structure and this is very useful as it solves a large part of the structure (six carbons in one shot).

Though these observations are really interesting, realize that for the organic chemist this sort of spectroscopy serves to identify the compounds. How do we know what we have – we take a picture of the molecules. How do we take a picture – IR and NMR spectroscopy (and other forms of spectroscopy).

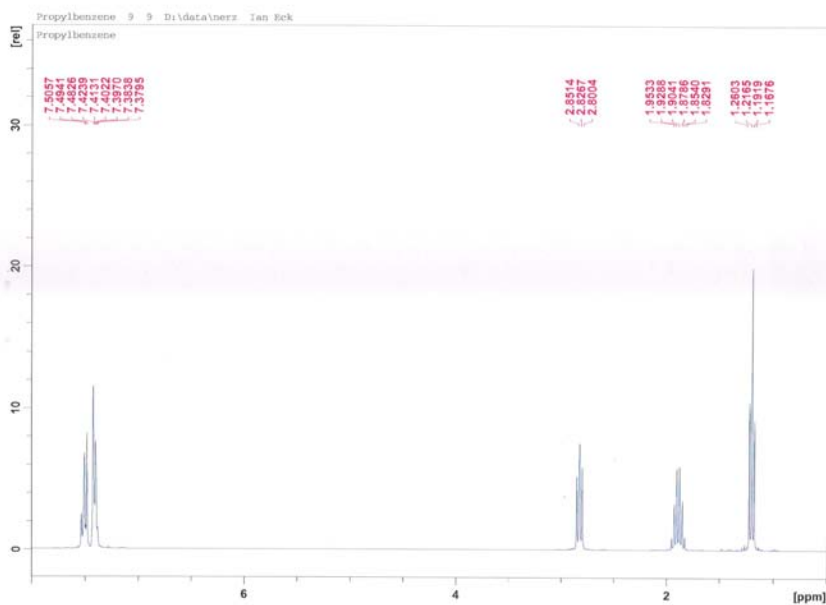
The hydrogens on the carbon next to the benzene ring are called benzylic hydrogens and like allylic hydrogens (next to double bonds), they are at around 2-2.5 ppm.



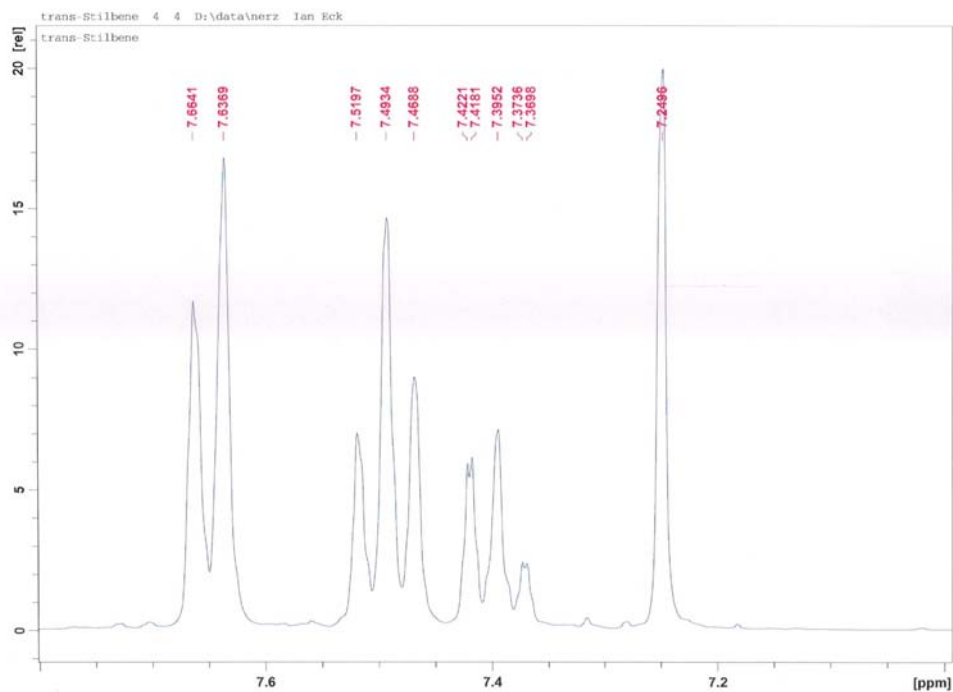
The rest of the molecule if an alkyl benzene should have features more or less like an alkane.

Please consider the proton NMR spectrum of propyl benzene given below.

Propyl benzene



Please study the spectrum of trans-stilbene given below.
trans-stilbene

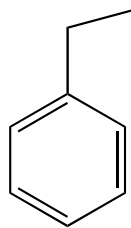


You should examine the same compound for which you studied the IR spectrum using the usual data base.

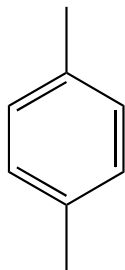
These compounds are ethylbenzene, isopropylbenzene, p-xylene, butylbenzene, bromobenzene.

Please link up using the data base.

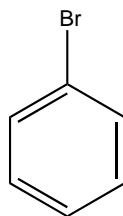
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi



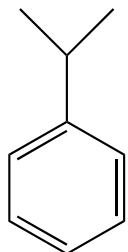
ethylbenzene



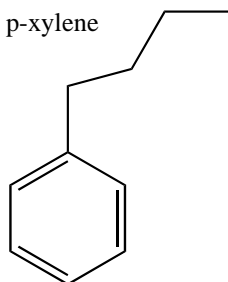
p-xylene



bromobenzene



isopropylbenzene



butylxylene

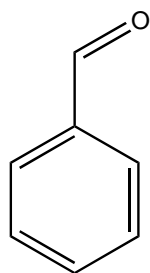
Please note again that the data base is very sensitive during the search process . If you make the slightest typo or syntax error, it will state it does not have data on the compound in question. Though all the compounds suggested in this text have been tested and the data base did have them, it is possible to have problems searching. For example, isopropylbenzene is listed as cumene. I would recommend if you are having trouble searching on the spectral data base, to enter the formula of the compound. Usually this will lead you to a more extensive list of isomers, but the desired compound will be recognizable .

Aldehydes

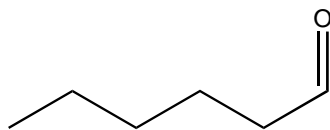
Infrared Spectra of Aldehydes

To get a feel for the infrared spectroscopy for aldehydes, link up to the following spectra of aldehydes on the normal spectral data base found on our website. You should look up benzaldehyde (we ran a spectrum and it is included), hexanal, 3-hexenal.

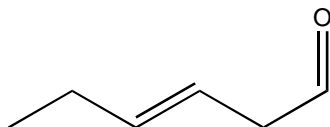
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi



benzaldehyde



hexanal



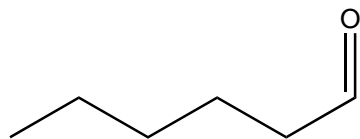
E-3-hexenal

The aldehyde groups has several expected absorptions in the functional group region. First and most obvious, would be the carbonyl. The carbonyl group is found in a number of functional groups. Like most carbonyls, they absorb at or around 1700 cm^{-1} . The absorption is a very strong, sharp absorption corresponding to the stretching vibration of the carbonyl group. The aldehyde is peculiar among the carbonyl containing functional groups in that it has a hydrogen directly bonded to the carbon of the carbonyl. The hydrogen is different from a typical hydrogen because it is bonded directly to the polar group. It actually gives two absorptions, one at approximately 2850 and 2750 cm^{-1} . This hydrogen is quite distinct from any other hydrogens in the molecule. Any other absorptions are in the fingerprint region. The rest of the molecule will give absorptions typical of the other groups covered in this text. For example, benzaldehyde would also exhibit the absorptions characteristic of an aromatic ring. It would have sp^2 C-H stretching just above 3000 cm^{-1} and C=C stretching vibrations from the aromatic ring at 1600 and 1500 cm^{-1} . Since it is aromatic it will also show the expected aromatic overtones described earlier. Remember to focus on the topography more than the numbers, but you might first use the numbers to get yourself oriented.

Link up with the IR spectra of hexanal on the website.

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

hexanal



Study this spectrum. Try to identify the features of the aldehyde (the C=O stretch and the C-H stretching vibration) group. In addition to this what would you expect? The rest of the molecule is fundamentally a hydrocarbon.

So you should expect to observe C-H stretching vibrations, sp^3 just below 3000 cm^{-1} and other than that, nothing extraordinary in the finger print region.

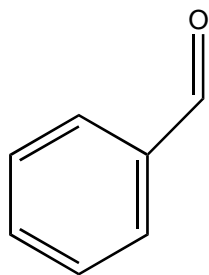
How would the IR spectrum of 3-hexenal differ from the last spectrum. It should have exactly the same features, except for the double bond. It is basically an aldehyde, hydrocarbon and an alkene. What would you expect to observe for an alkene? sp^2 C-H stretching just above 3000 cm^{-1} and you would expect to see the double bond stretch at around 1660 or 1640 cm^{-1}

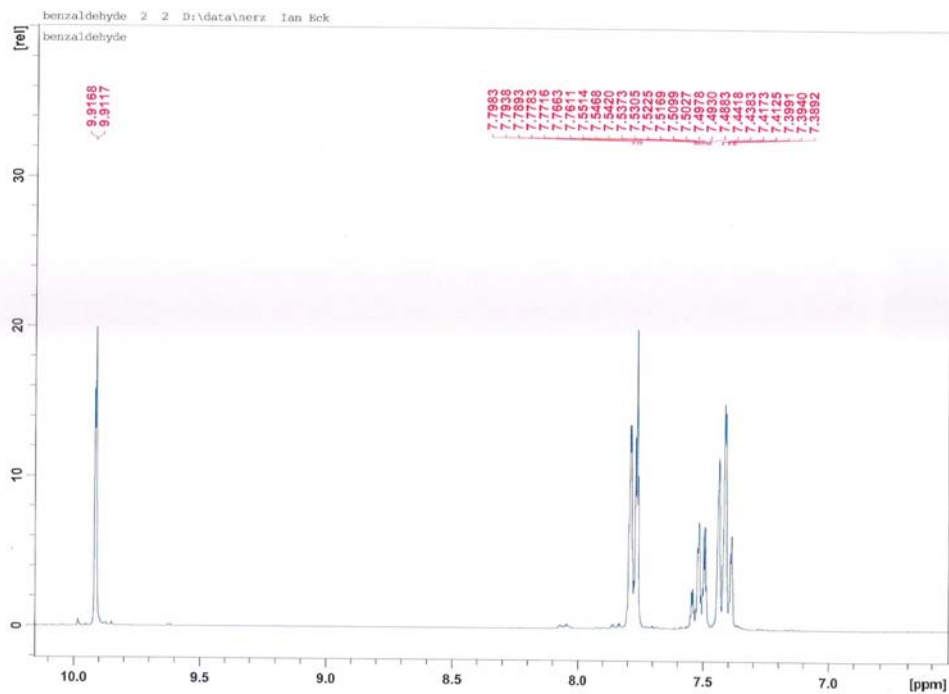
1H NMR of aldehydes

The distinctive feature of an aldehyde in the proton NMR spectrum is the hydrogen on the carbon in the carbonyl. It is at a very uniquely position that is approximately in the range from 9.5 to 10 ppm. It is one of the highest frequency positions in the proton NMR spectrum. Other than that, the rest of the spectrum would exhibit the features typical of the functional groups in the structure. So for benzaldehyde, one would expect a peak or peaks for the aromatic hydrogens which would be around 7 ppm. Predict what you would see for the following compounds and then check them on the website.

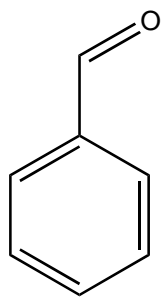
The Proton NMR Spectrum of Benzaldehyde is included below for your study:

Benzaldehyde

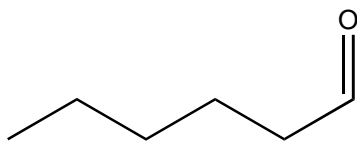




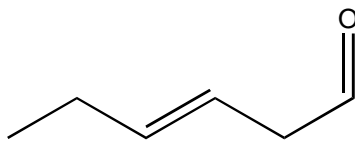
Please link up to the proton NMR spectra of hexanal, 3-hexenal and any other aldehydes you choose to study.



benzaldehyde



hexanal



E-3-hexenal

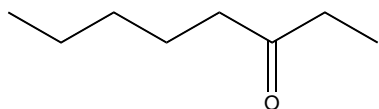
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Ketones

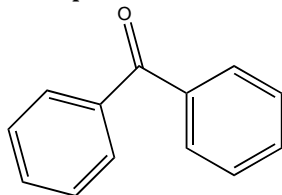
Infrared Spectra of Ketones

One would expect two distinct features in the functional group region of the infrared spectrum. The carbonyl of a ketone (similar to an aldehyde) would have an absorption at or around 1700 cm^{-1} . It should be strong and sharp. The rest of the IR would look like a typical hydrocarbon unless it has other functional groups. The other functional groups, if present, would have the characteristics of those functional groups presented elsewhere in this text. Predict the major infrared characteristics in the functional group region for the following ketones: 3-octanone, acetophenone, and benzil. The following are the structures of these compounds.

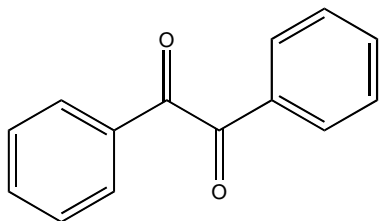
3-octanone



acetophenone

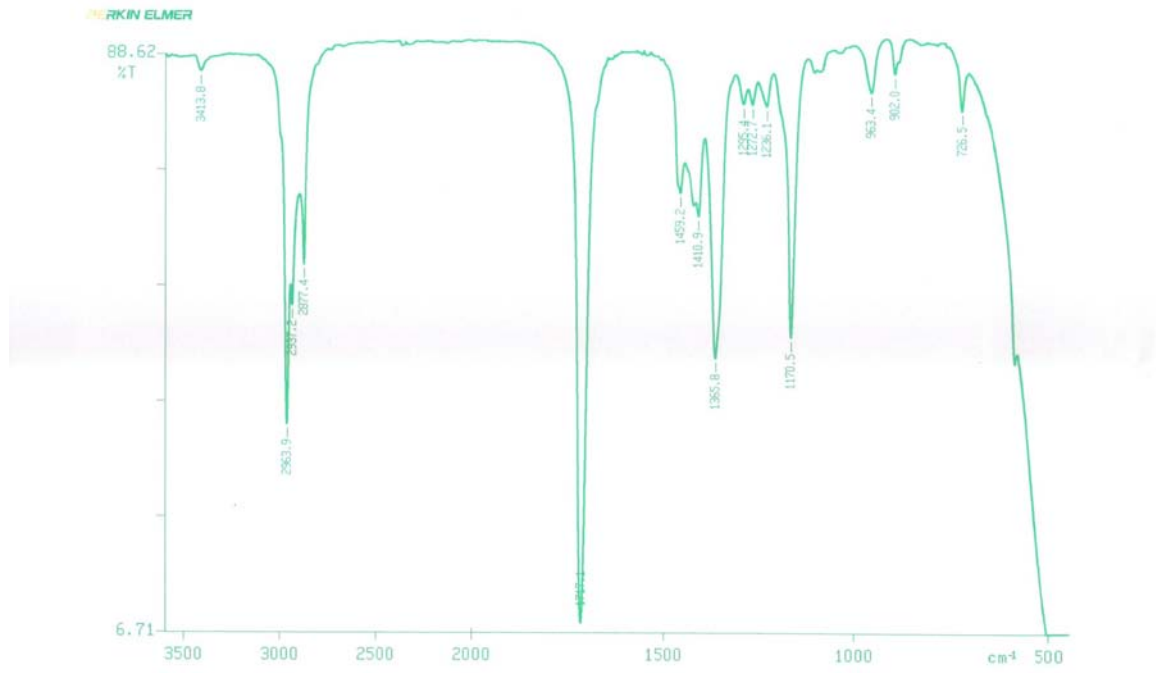


benzil



Please consider the IR spectrum of 2-pentanone given below:

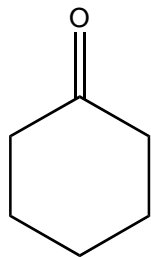
2-pentanone



10/03/26 11:36 rosaff-mohan-zinn
X: 1 scan, 4.0cm-1

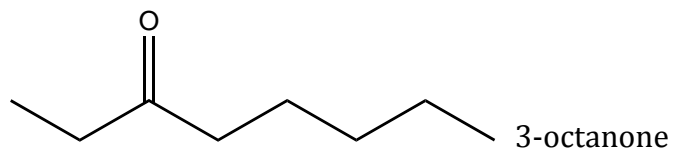
Please consider the IR spectrum of the cyclohexanone compound below.

Cyclohexanone



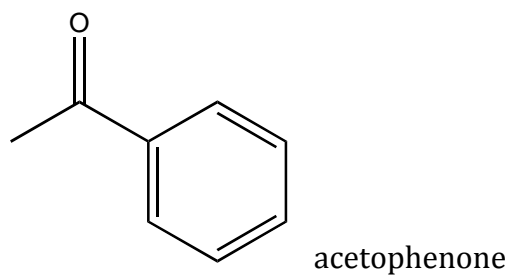
Please study the IR spectrum for the compound below of acetone.

Please link to the IR spectrum of 3-octanone below.



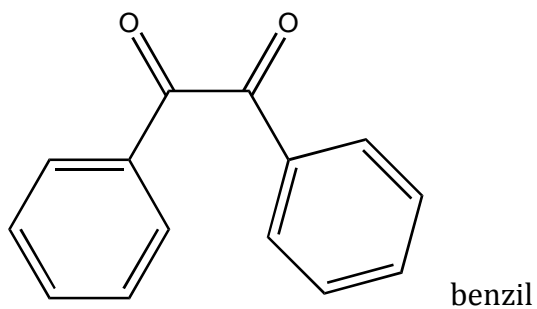
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Please link to the IR spectrum of acetophenone below.



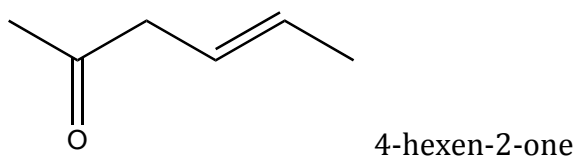
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Please link to the IR spectrum of benzil below.



http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Please link up to the IR spectrum of the compound below.



http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

When one co, one would expect a peak at around 1700 cm^{-1} for the carbonyl and a peak at just below 3000 cm^{-1} for the sp^3 C-H bonds. That is all that should appear in the functional group region. For acetophenone, one would expect the additional stretching vibration absorptions due to the aromatic ring. So we would expect the carbonyl at 1700 cm^{-1} , the sp^3 CH stretching from the methyl group and the sp^2 aromatic stretch from the C-H groups on the aromatic ring as well as the ring vibrations themselves at 1600 cm^{-1} and 1500 cm^{-1} . One would expect benzil to be somewhat like acetophenone, minus the sp^3 C-H because there is none, however, if you observe this spectrum on the data base, you will see that there are two carbonyl absorptions at around 1700 cm^{-1} this is typical of diketones. The last compound which has aspects of a ketone, an alkene and an alkane, should show all three characteristics. The sp^3 C-H is just below 3000, the carbonyl at 1700 cm^{-1} and the alkene at 1640 or 1660 cm^{-1} . The alkene will also have sp^2 C-H stretching vibrations that are just above 3000 cm^{-1} . Hopefully from all this study, you are learning your functional groups and you are starting to know the landscape of the various groups.

In addition to looking up every compound assigned here, study the IR of all the compounds listed on the survey of functional groups.

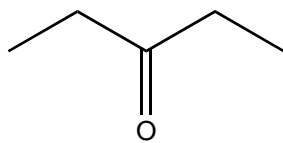
^1H NMR

The ketone group has no hydrogens so it will not show up directly in an NMR. One would expect the NMR of 3-octanone shown above to have features of an alkane for the most part, but it is true that hydrogens that are right next to the carbonyl, i.e., on the carbon on either side of the carbonyl are at slightly elevated field positions, so you will see these at around 2-2.5 ppm. Look up this compound and try to find this feature. Now a peak or group of peaks at this position does not guarantee you have a ketone, but it is certainly supportive of this sort of structure.

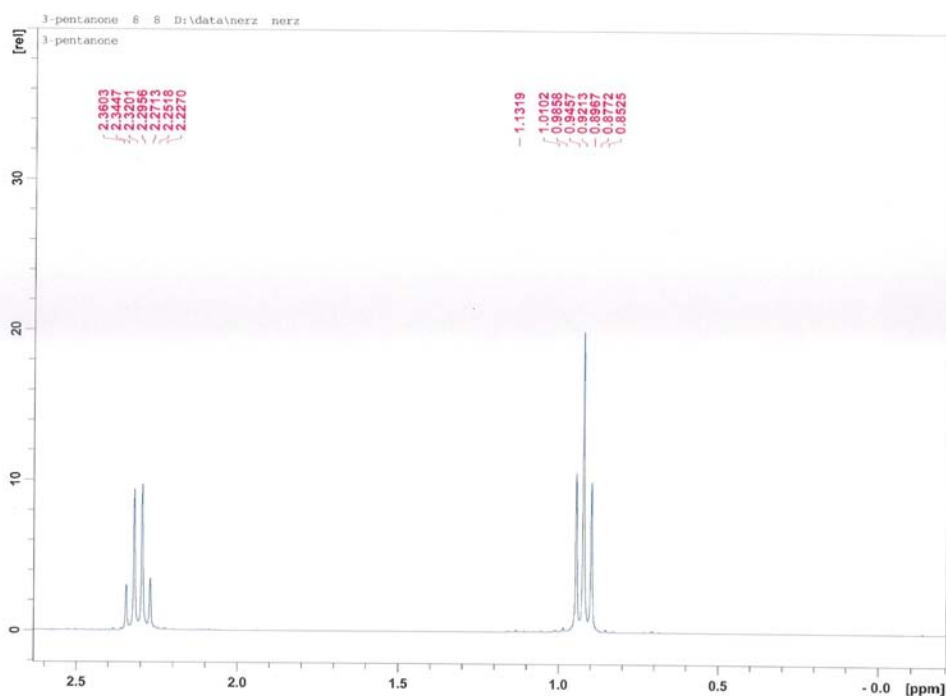
The other compounds shown above should show the feature discussed in the paragraph above, but also any other features of any functional groups listed. Of course, alkane sections of the molecules will be around 1 ppm with splitting when different hydrogens are near each other. The acetophenone should have peaks between two and three for the methyl hydrogens which are right next to the carbonyl and peaks around 7 ppm for the aromatic hydrogens. Benzil should only have aromatic hydrogens. The last compound will have features of both a ketone and an alkene in that the hydrogens on the alkene will be at five ppm and the hydrogens flanking (on the adjacent carbons to the carbonyl, aka allylic) the carbonyl will be in the 2-3 range. Hydrogens flanking or allylic to a conventional carbon-carbon bond double bond will also be in this range. Anything purely alkane in nature will absorb in the region around 1 ppm (0.8-1.3).

Remember, the goal here is to study, get a sense of the generally landscape. Hopefully, at the end of this exercise you can look at a spectrum and state what kind of compound it probably is.

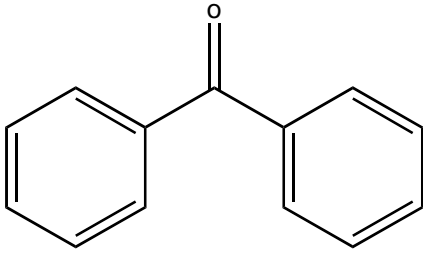
Consider the proton NMR of 3-pentanone shown below.



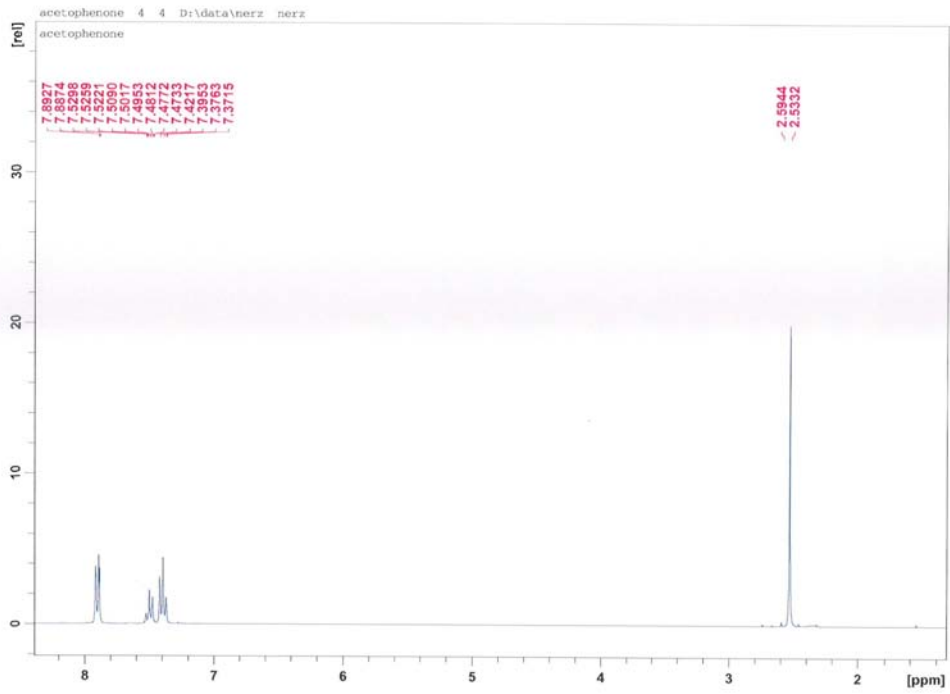
3-pentanone



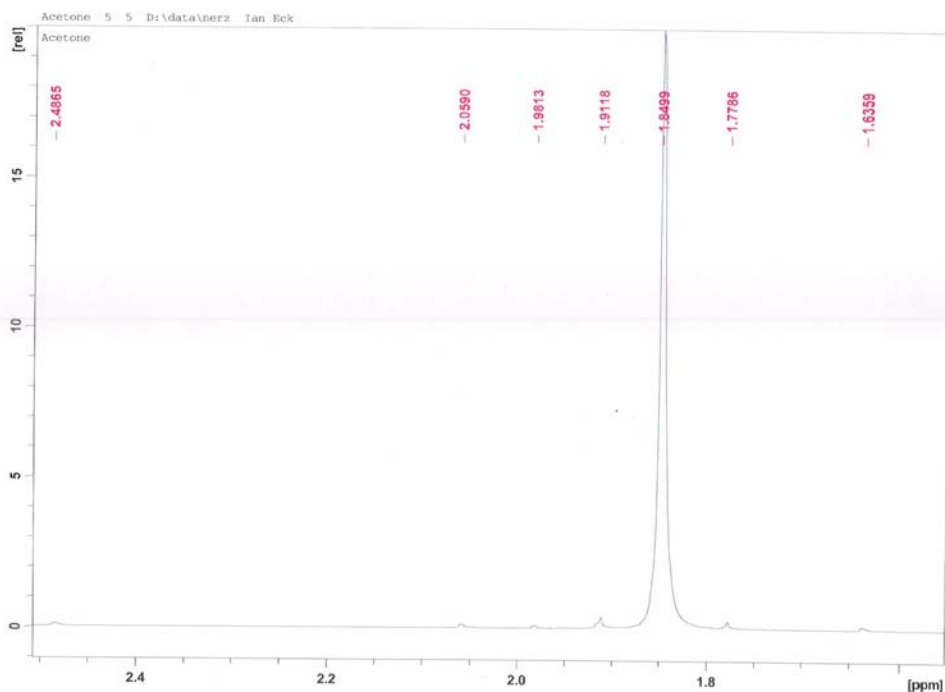
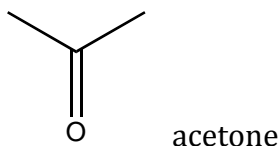
Please study the proton nmr spectrum of acetophenone below.



acetophenone



Please consider the proton NMR of acetone shown below.



Carboxylic Acid Derivatives.

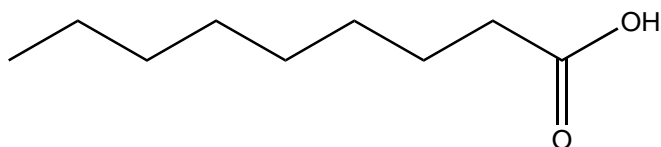
Carboxylic Acids IR spectrum

In the functional group region, the IR spectrum will have absorptions due to the carbonyl – again sharp, strong around 1760 cm^{-1} and a peak due to the OH. The OH absorption does not look like a hydroxyl in that it is extremely broad and quite intense compared with a normal alcohol peak. Occasionally, it will appear to be

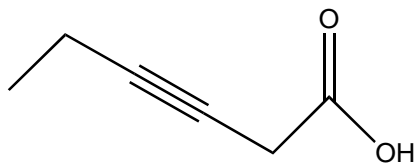
overall less intense. It is very broad overall and contains spikes as well and at most extends to fifty percent of the total intensity (this means it looks like a wide broad hump with spikes in it – not going so far down the page) . It is so broad it can extend from about 3300 cm^{-1} or so all the way to 2500 cm^{-1} or so. Carboxylic acids have a very distinctive landscape and are really worth looking. Normally you can't miss a carboxylic acid on an IR spectrum. There is also a C=O bond in the functional group, but this does not show up in the functional group region, this shows up in the fingerprint region and is at or around 1100 cm^{-1} . Once again, any other functional groups would show the characteristics of the other functional groups more or less independently of this functional group. The more you review this the better. So look up and study the spectra of nonanoic acid, 2-hexynoic acid, 3-heptenoic acid, benzoic acid.

Please link with the listed molecules using the following website.

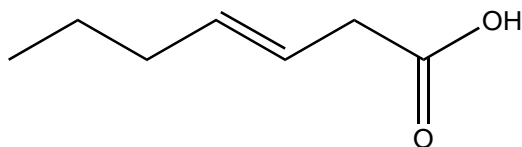
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi



nonanoic acid



2-hexynoic acid



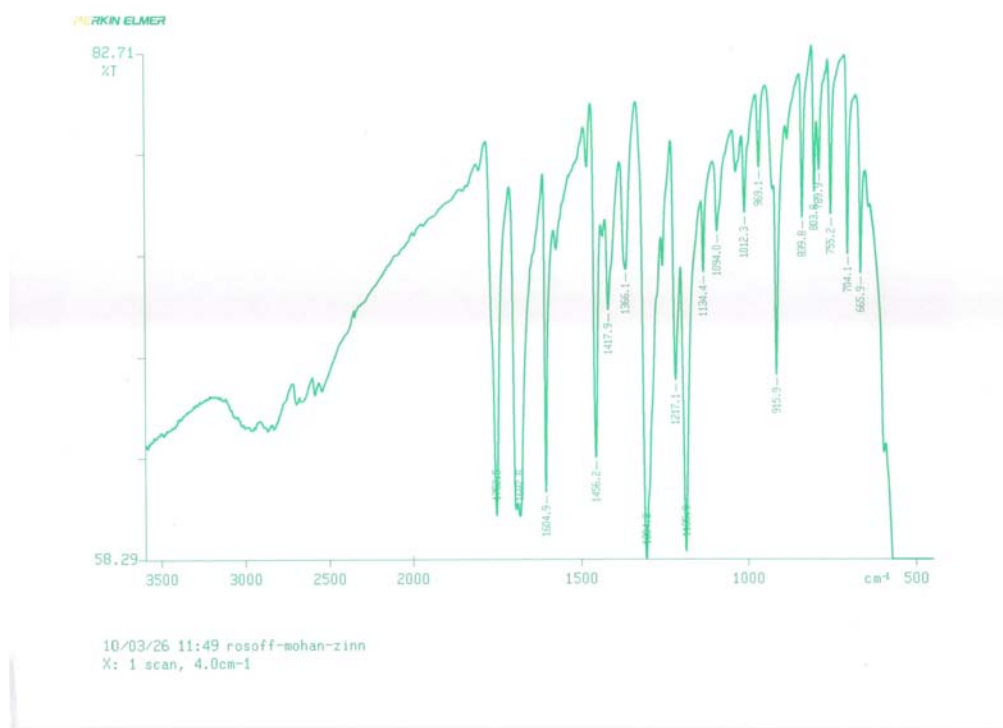
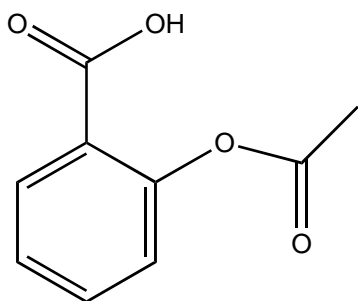
3-heptenoic acid

Nonanoic acid should only show the features described above for a carboxylic acid. The rest of the molecule would give features of an alkane. Can you find the peaks corresponding to these features? We have not looked at an alkyne for a while. In

addition to the carboxylic acid features, you should see a triple bond absorption at around 2200 cm^{-1} . Can you find it? Sometimes these are weak. Why? Since this triple bond has no hydrogens on it there will be no sp C-H absorption. The rest will be similar to an alkane.

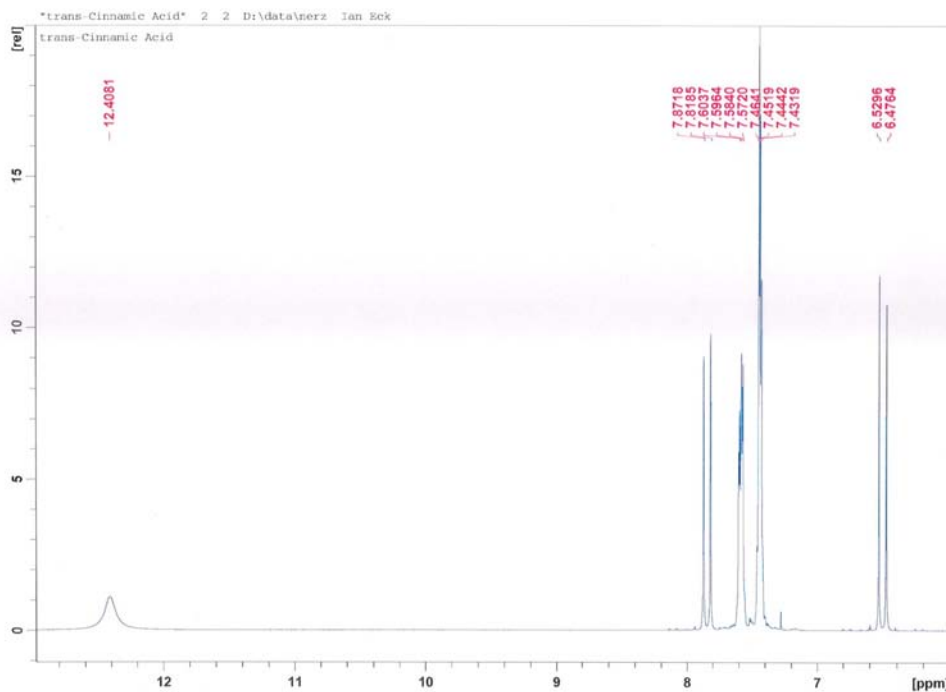
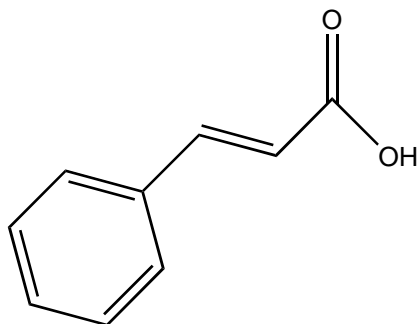
In regard to 4-heptenoic acid, it will have the carboxylic acid features, the alkane and the alkene features. Please find all of these in the functional group region. Benzoic should reflect carboxylic acid and aromatic features.

Please study the IR of Acetyl salicylic acid given below

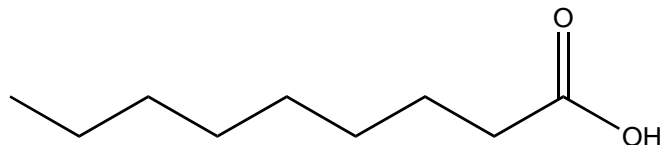


^1H NMR of Carboxylic Acids

Please study the proton NMR features of in the functional group region of trans-cinnamic acid. The only part of the structure that would be unique to the carboxylic acid via NMR is the OH which absorbs at or around 12 ppm. These peaks tend to be broad as observed in the spectrum of trans-cinnamic acid. Other than the OH, the hydrogens that are allylic to the carbonyl will be at or around 2-3 ppm. It is similar to hydrogens being adjacent to any carbonyl, such as a ketones.



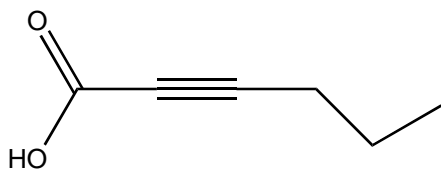
Please link into the proton NMR spectrum of nonanoic acid.



nonanoic acid

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

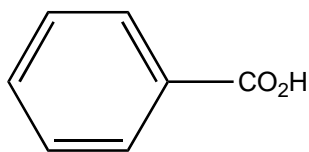
Please link into the proton NMR spectrum of 2-hexynoic acid.



2-hexynoic acid

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Please link into the proton NMR spectrum of benzoic acid.



benzoic acid

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

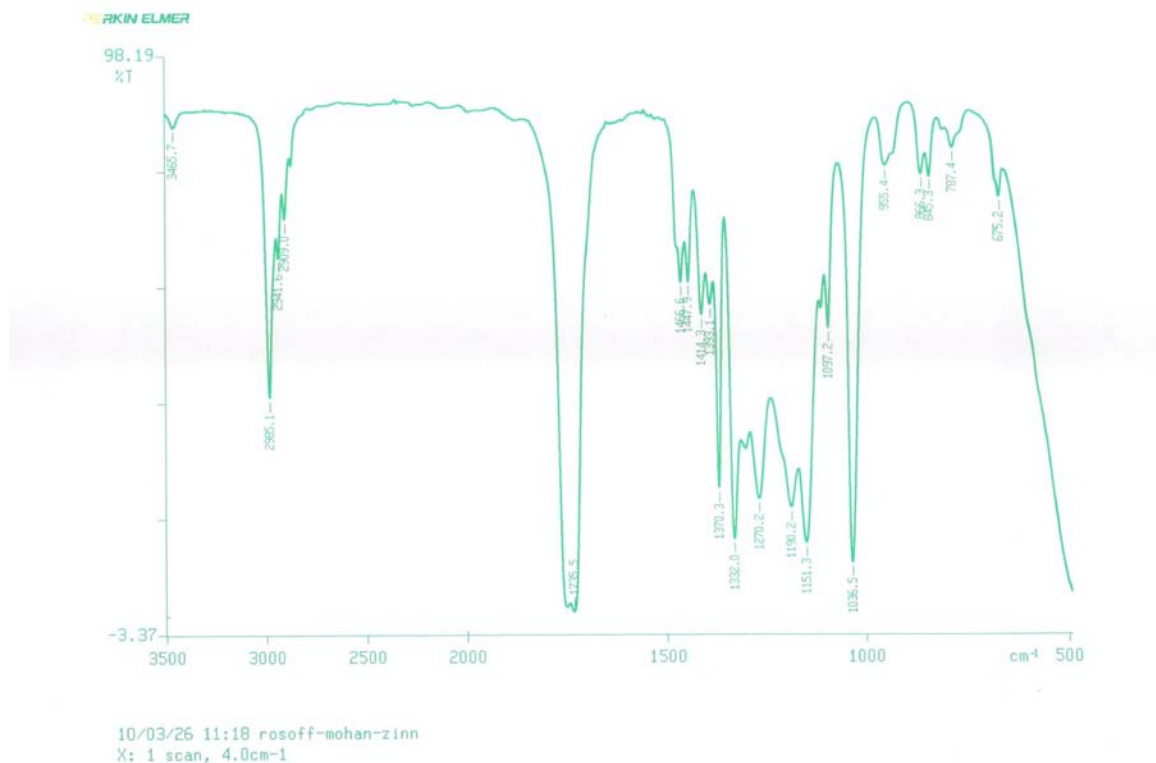
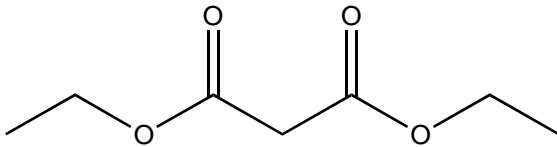
Esters

Infrared Spectroscopy of esters

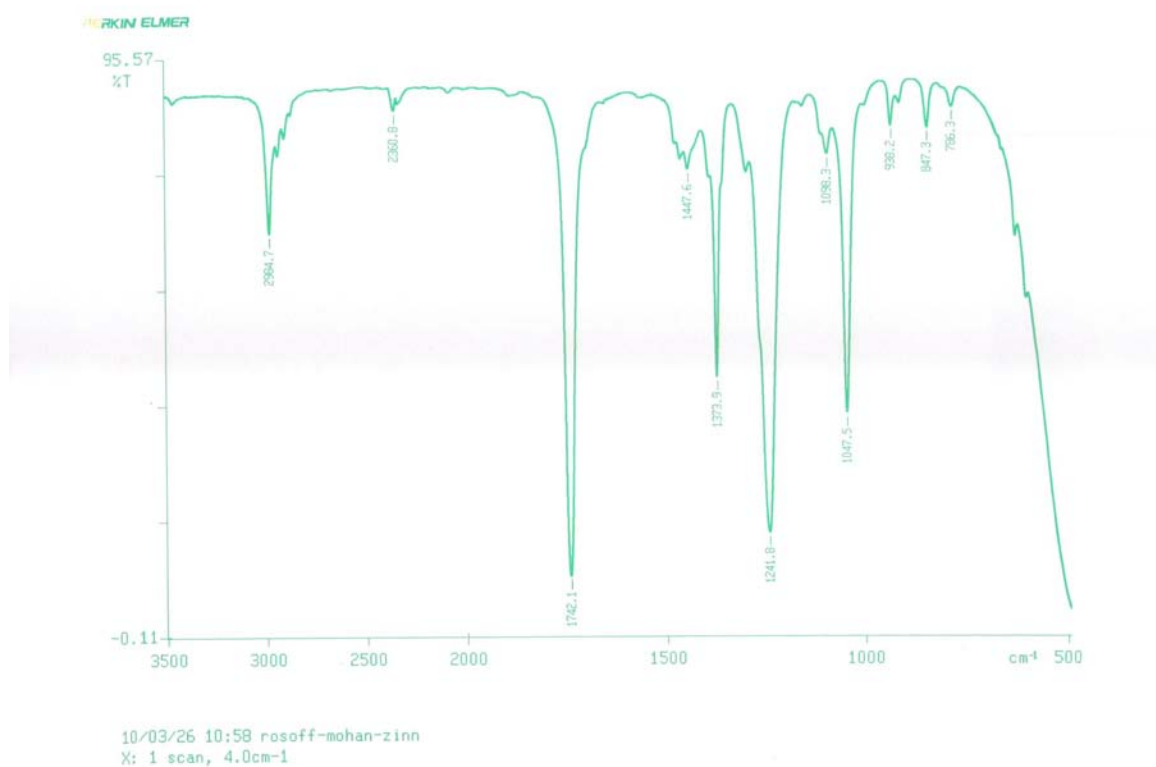
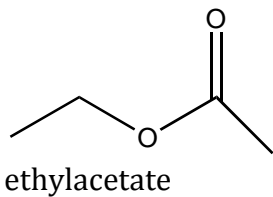
What would you expect for the functional group region of a typical ester in the functional group region of the IR? It has a carbonyl, so you would expect the absorption at approximately 1740 cm^{-1} . It also has single bond C-O bonds and these occur in the fingerprint region. Therefore, the only manifestation of the functional group should be in the functional group region at around 1700 cm^{-1} (it actually is above 1700 cm^{-1}), but in the following compounds, look for the strong, sharp peak at around 1740 cm^{-1} . It will have features of a hydrocarbon, in that like all organic compounds it will have a peak just below 3000 cm^{-1} due to the (yes, you can recite it in your sleep now) – due to the sp^3 C-H stretching vibration.

The spectrum would also contain any features we have discussed for other functional groups and portions of the molecule.

Please study the IR spectrum of diethyl malonate.
Diethylmalonate

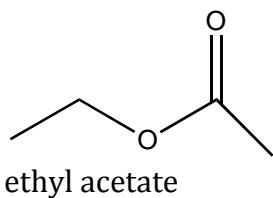


Please study the IR spectrum of ethyl acetate shown below.



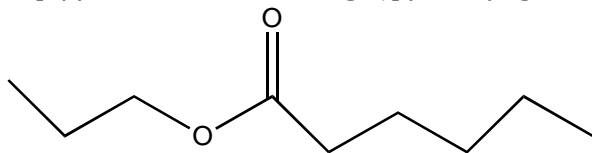
Using the following structures, please predict what you would expect in the functional group region of the infrared spectrum for the following compounds. .

Ethylacetate, propylhexanoate, methylbenzoate, ethyl-2-butenolate

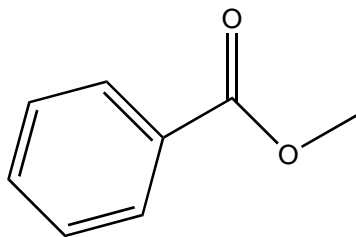


Please find the IR spectrum of the following compounds on our normal website.

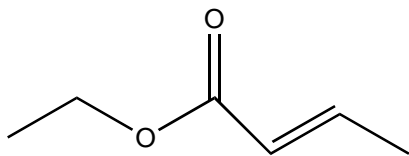
http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng



propylhexanoate



methyl benzoate



Link in to the spectra for the above compounds using the following data base.

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

As an example, please consider E-ethyl-2-butenonate. What would you expect? Starting at the highest frequency end of the spectrum, there should be sp^2 C-H stretching just at or above 3000 cm^{-1} , then there should be sp^3 C-H stretching just at or below 3000 cm^{-1} . Then at around 1700 cm^{-1} (1700 cm^{-1} is being used generally to describe the position of carbonyl groups in general, though they appear at arrange of positions, depending on functional groups) one would expect a strong, sharp peak due to the C=O stretching vibration due to the carbonyl and finally there should be a peak at or around 1640 cm^{-1} for the double bond. In fact, in this case the double bond would absorb a little lower in frequency due to the conjugation (to be discussed in class – resonance). Conjugation lowers the position of double bonds in general as will be discussed in lecture.

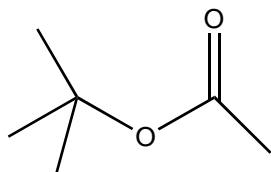
¹H NMR Spectroscopy of Esters

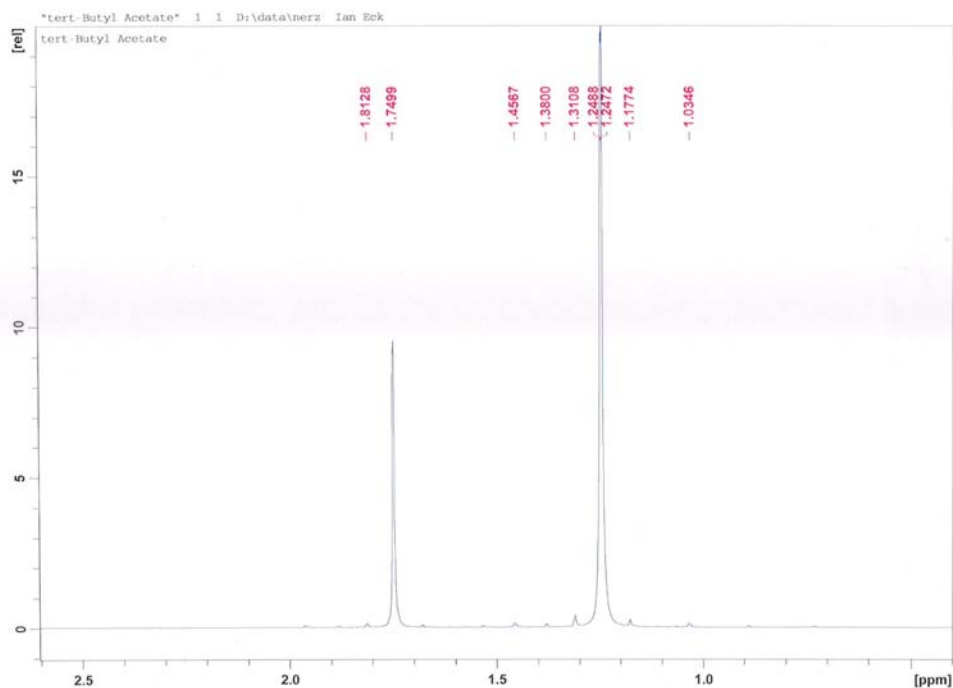
Like the ketone, the NMR of ester shows no direct evidence of the ester functional group as the hydrogens are not directly attached to the heteroatom, oxygen,

however, the positions of the hydrogens on the carbon next to the carbonyl are found in the 2-3 ppm range as discussed for the ketone and the hydrogens on the carbon attached to the oxygen are at 3-4 ppm. Which hydrogens are closer to oxygen? Count the bonds to the oxygen in each case. The hydrogens on the ether-like carbon are two bonds from oxygen and the hydrogen on the carbon next to a carbonyl are three bonds from oxygen. These latter hydrogens could be classed as allylic hydrogens. The closer the oxygen is to the oxygen, bondwise, the higher the position in the NMR.

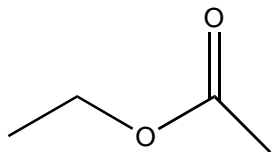
Please consider the proton NMR spectrum of tert-butyl acetate given below. Before analyzing it, consider what absorptions you would expect for tert-butyl acetate. Does the spectrum meet with your expectations.

tert-butyl acetate

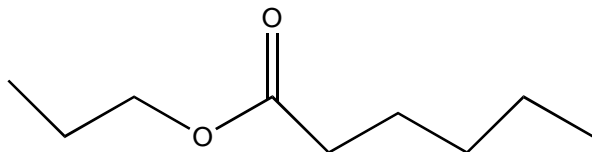




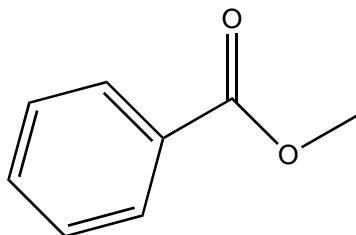
Please predict what you would expect in the proton NMR spectrum of the following compounds. Remember in proton NMR the only part of the compound observed are the hydrogens. What are the important features of an ester in the NMR? Once again, there are no hydrogens really on the functional group itself so one would only expect “dramatic”, well not so dramatic positioning of the hydrogens that are allylic to the carbonyl and two bonds from the single bonded oxygen. The allylic hydrogens (those on carbon attached to the carbonyl) should be at or around 2-3 ppm. The hydrogens on the carbon attached to the oxygen will be observed at approximately 3.5-4 ppm. Splitting will be observed if there are hydrogens on adjacent carbons. The rest of the structure will appear as an alkane. Can you find the outlined features in the following molecules?



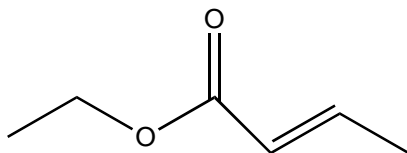
ethyl acetate



propyl hexanoate



methyl benzoate



E-ethyl butenoate

Again, the spectra for these compounds can be obtained from the following website (you should know where it is by now!!!!).

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

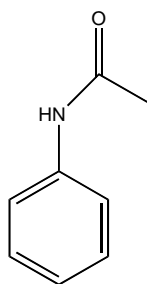
Amides

Infrared Spectroscopy of Amides

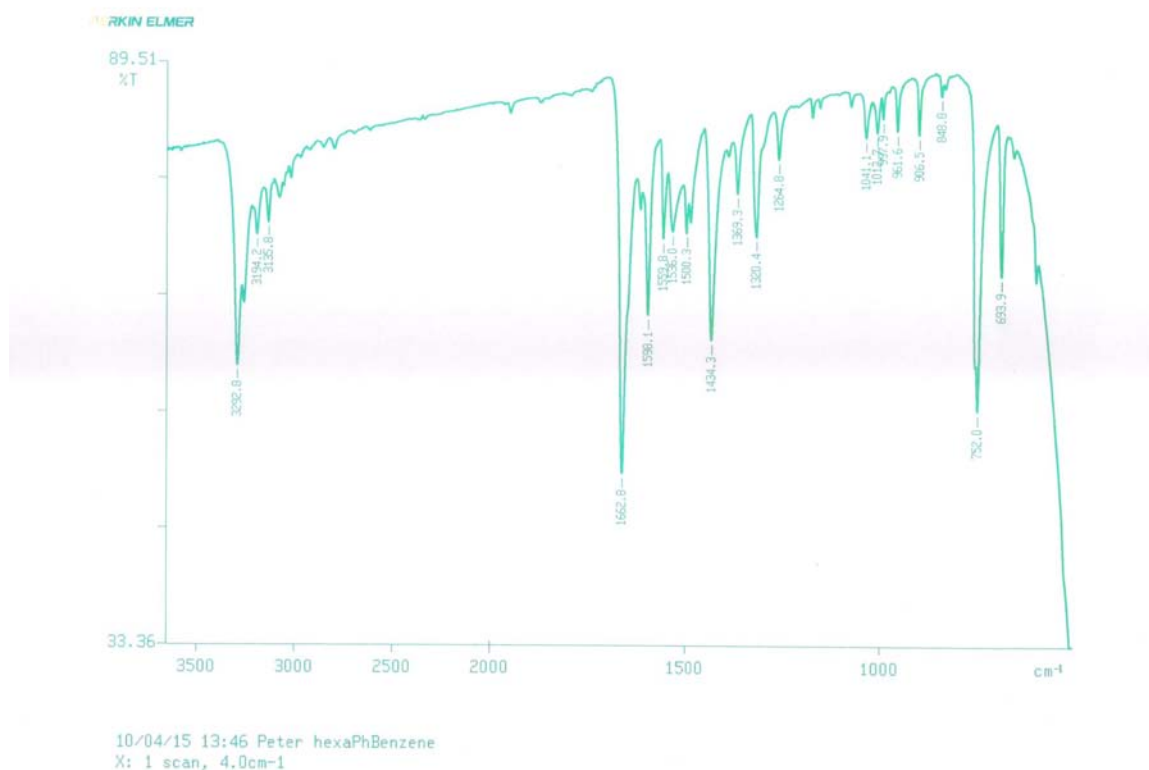
The important part of the infrared spectrum in terms of the functional group region is the carbonyl group and any absorptions due to the N-H bonds of the amide. Due to resonance stabilization from the donation of the lone pair into the double bond of the carbonyl, the carbonyl bond has more single bond character than a normal carbonyl and consequently is found at a lower position or frequency (wavenumber) than a normal carbonyl. Where a typical carbonyl might be at around 1700 cm^{-1} or above, an amide carbonyl is at approximately 1660 or 1680 cm^{-1} .

Consider the infrared spectrum provided below for acetanilide. The structure of acetanilide also provided below. What would you expect for this compound? You

would expect sp^2 C-H stretching. Why? Can you find this? You would expect sp^3 C-H stretching. Why? Can you find this in the spectrum? From the amide functional group, you would expect N-H stretching vibration which would be at about 3300 cm^{-1} and the carbonyl which due to the resonance delocalization of the lone pair, would be just below 1700 cm^{-1} . Can you find all these absorptions? You should look up other amides on the internet site http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi to practice and gain familiarity with the landscape. Note: amides have varying number of groups on the nitrogen. If the nitrogen is completely occupied by alkyl groups, then there should be no N-H groups, however, if one looks at N, N-dimethylformamine, one observes a big peak at 3500 cm^{-1} . One can take this as a contaminant, possibly water. DMF is very likely to be contaminated with water. Please consider the IR spectrum of acetanilide given below.



Acetanilide



Amides

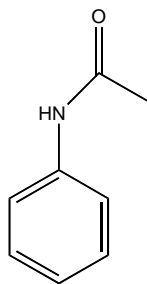
NMR Spectrum of Amides

What would we expect for the NMR of an amide? If there are no hydrogens on the nitrogen, the molecule should appear as a hybrid between an amine and a ketone perhaps. Sort of like an ester. So the hydrogens are next to a carbonyl they should be around 2-3 ppm and if the hydrogens are next to a nitrogen, they should be around 3-3.5 ppm. If on the other hand, there are one or two hydrogens on the nitrogen, the shifts are in the 4-8 ppm range.

Can you roughly predict the proton landscape for acetanilide, using our favorite website.

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng

Acetanilide



Acid Anhydrides

What would you expect for the remaining functional groups that we study in a typical organic chemistry course in regard to IR and NMR spectroscopy, i.e., acid anhydride, acyl halide or acid halide and nitrile.

Link in to the functional group worksheet to get some ideas about structures and names, make your predictions about the functional group regions of the IR and proton NMR and then verify your predictions by studying spectra as you have been rigorously trained to do through this exercise.

Unsaturation Number

This reading is the beginning of study of learning how to fully interpret spectra and solving the structure of unknowns using spectroscopy. In the problems that follow, you will have formula for the unknowns. The formula of a compound itself contains important structural information. To extract the information contained within the formula, it is useful to calculate what is often called the unsaturation number. It has also been called the index of hydrogen deficiency, $r+pi$, among other names. Your current text, uses a formula which you are invited to utilize if it suits you. It works perfectly, but personally, I prefer a different method which will be detailed in the following text.

The unsaturation number is a comparison of the formula of an unknown compound (connectivity unknown) with the formula of a theoretical saturated formula that has the same number of carbons and heteroatoms (atoms other than our favorites, carbon and hydrogen). The key is to know how to calculate the saturated formula. Let us begin with an example. Supposing one had an unknown compound with the molecular formula C_7H_8 . If you consider this formula compared to an alkane with seven carbons, it has a reduced number of hydrogens. With the given formula, the compound can't have any of the functional groups we have discussed that contain oxygen, nitrogen or halogen. Why? The molecule can only be an alkene, alkyne or aromatic. Why? Now what we need to do is come up with the theoretical unsaturated formula. This is done by considering the formula for alkanes C_nH_{2n+2} . For a compound with seven carbons the formula would be C_7H_{16} . Our formula has only 7 carbons, so the saturated

formula is based on seven carbons. If every possible slot for a compound with seven carbons was filled with hydrogen it would have 16, however, we only have 8 hydrogens in our unknown. This means that the compound is deficient by 8 hydrogens or 4 pairs. Every double bond results in the loss of one pair of hydrogen. Every triple bond results in the loss of two pairs of hydrogen. Every ring results in the loss of a pair of hydrogens. You might want to use models or structures to make sure that you understand these ideas about hydrogen loss. What does the fact that this unknown is missing two pairs of hydrogens say about the structure. This hydrogen deficiency is telling us that it must have in its structure functional groups that are hydrogen deficient such that the total of the deficiency adds up to eight hydrogens or four pairs. Remember we can't use oxygen, nitrogen or halogen in building this deficiency. Our molecules must contain rings, double bonds and or triple bonds. To have a total unsaturation of four, we could have four double bonds (each a loss of two hydrogens) or we could have one ring and three double bonds, we could have two triple bonds, etc. Is this making any sense? Again, if you are having trouble with this idea of certain functional groups resulting in the loss of pairs of hydrogen, you should take your models out and build a ring, a double bond or a triple bond and you will quickly discover that you have to remove hydrogens to make these functional groups. Compounds generally missing pairs of hydrogens compared with the saturated formula is called unsaturation. However, the term unsaturated fat refers to fat that has one or more double bond in the fatty acid chains.

Draw four distinct isomers of C_7H_8 below.

See video link for solutions to problems.

Oxygen does not change the saturated formula, though it can be a part of a functional group that is unsaturated. For example, a carbonyl has an unsaturation number of one, meaning it is missing one pair of hydrogens. Consider the following formula. $C_8H_{10}O$. The theoretical saturated formula used for comparison sake is $C_8H_{18}O$. Notice I did not do anything with the oxygen. Once again my unknown is missing four pairs of hydrogens. Draw some structures that work for this formula in the space below.

See video link for solution to this problem.

In regard to unsaturation number, nitrogen and halogen are a different story. Because nitrogen is trivalent you need to add one more hydrogen to the theoretical saturated formula for every nitrogen in the structure. Being trivalent means there is an extra slot for hydrogen. So for example, supposing, you have the formula $C_6H_6N_2$ as your unknown. What would the saturated C_nH_{n+2} formula be? You should have obtained a value of $C_6H_{16}N_2$

or the saturated . What I did was use the formula but then added two more hydrogens on for each nitrogen in the real formula. After doing this compare the two formula. The unknown has a 10 fewer hydrogens than the theoretical saturated formula. Again note, the theoretical saturated formula, has every hydrogen it can possibly have without any multiple bonds or rings. Ten missing hydrogens means we have to have functional groups that result in a deficiency of five pairs of hydrogens. What combinations of unsaturated functional groups could be combined to add up to five. Don't forget the nitrogens could be involved. Consider the nitrile groups discussed above. How many pairs of hydrogen have to be sacrificed for the nitrile functional group?

Try to write five structures for the unknown that are diverse in nature in the space below that have the formula given, i.e., $C_6H_6N_2$.

See video link for solutions to the problem.

Finally, in calculating the unsaturation number, the halogen is also peculiar. Think about it, being monovalent, it takes the place of a hydrogen in a structure. So, you have to subtract one hydrogen from the theoretical formula for every halogen in the actual or unknown formula. So for example, suppose the unknown is C_9H_7Cl . In this case to write the theoretical, saturated formula, you would need to use the normal C_nH_{2n+2} with the correction for chlorine. It would be C_9H_{20} , but because of the presence of chlorine the substrate would become $C_9H_{19}Cl$. Notice again, the chlorine is taking the place of the hydrogen. Taking the difference between the , the difference is 12 so this compound has the extraordinary unsaturation of 6 pairs. You might note at this point (this can be applied to the prior exercises) that benzene rings have an unsaturation of four (this is a great way to chew up four pairs of hydrogens!). Why? This is because a benzene ring is in essence three double bonds and a ring. Think about it. Look at the aromatic rings up above in this presentation.

Try to write six structures that have the formula C_9H_7Cl . Make the structures diverse and note that the halogen always has to be peripheral, it can't be a part of any of the unsaturation substructures. It is its nature as a monovalent element like hydrogen.

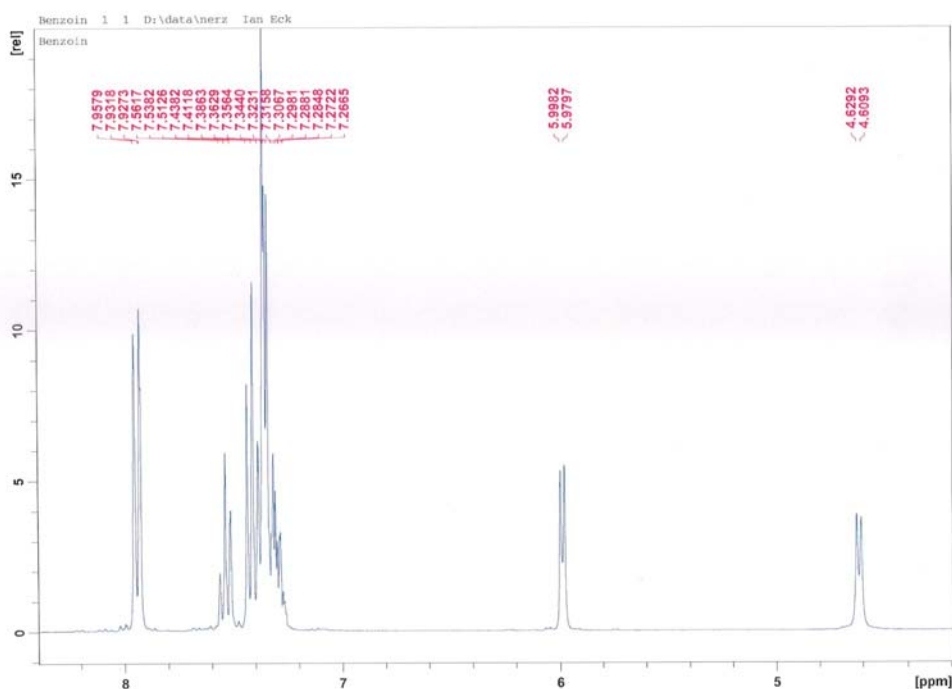
See video link for solutions to these problems.

You should not be bogged down in this exercise or in any of the above counting hydrogens. **There is no need to count hydrogens (not angry, just emphatic).** You should be using the bond line notation shown in class and trying hard not to count hydrogens. If your molecule has say two triple bonds, a double bond and a ring and the correct number of carbons and heteroatoms, it is the right compounds. The number of double bonds and rings and triple bonds automatically sets the number of hydrogens which of course, do not need to be drawn in on a structure.

Problem 1

The following is a problem. You should calculate the unsaturation number, so you have some idea about what elements should be present in general and then study the functional group region of the spectrum to see if you can come up with a structure or structures that would work. Write down your idea. Note in the IR it has a very strong, broad peak at 3400 cm⁻¹

Problem: C₁₄H₁₂O₂

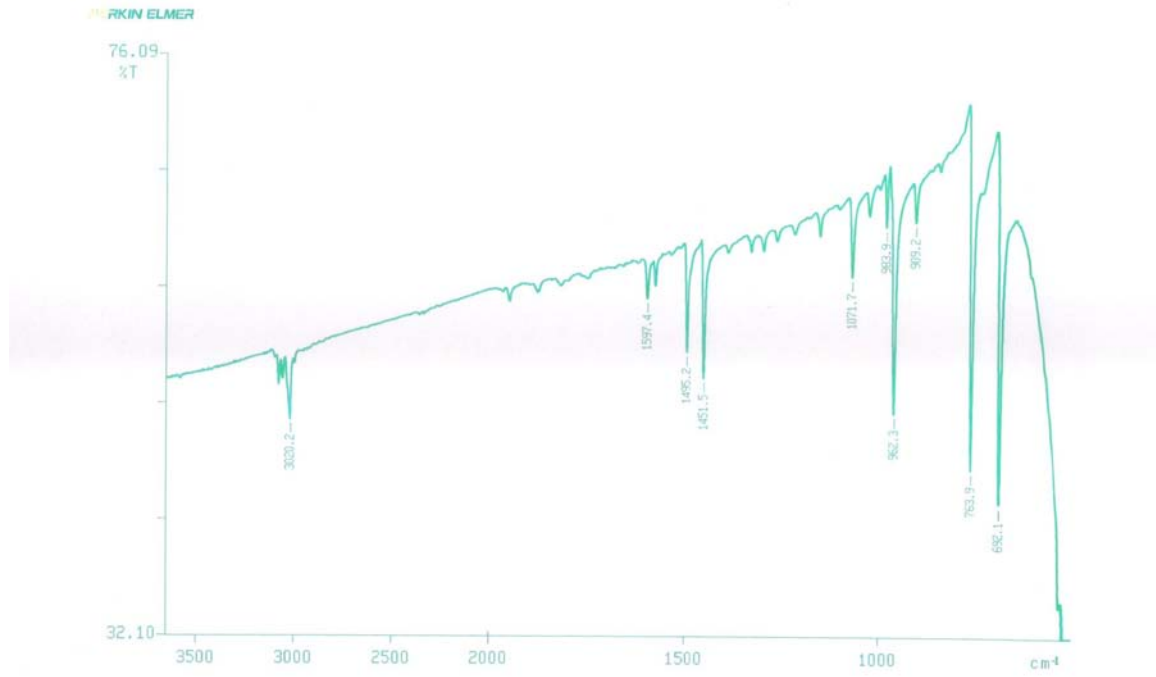


Try to write a structure or structures that work for this compound. You don't have to come up with the exact structure.

Please see the video link for solution.

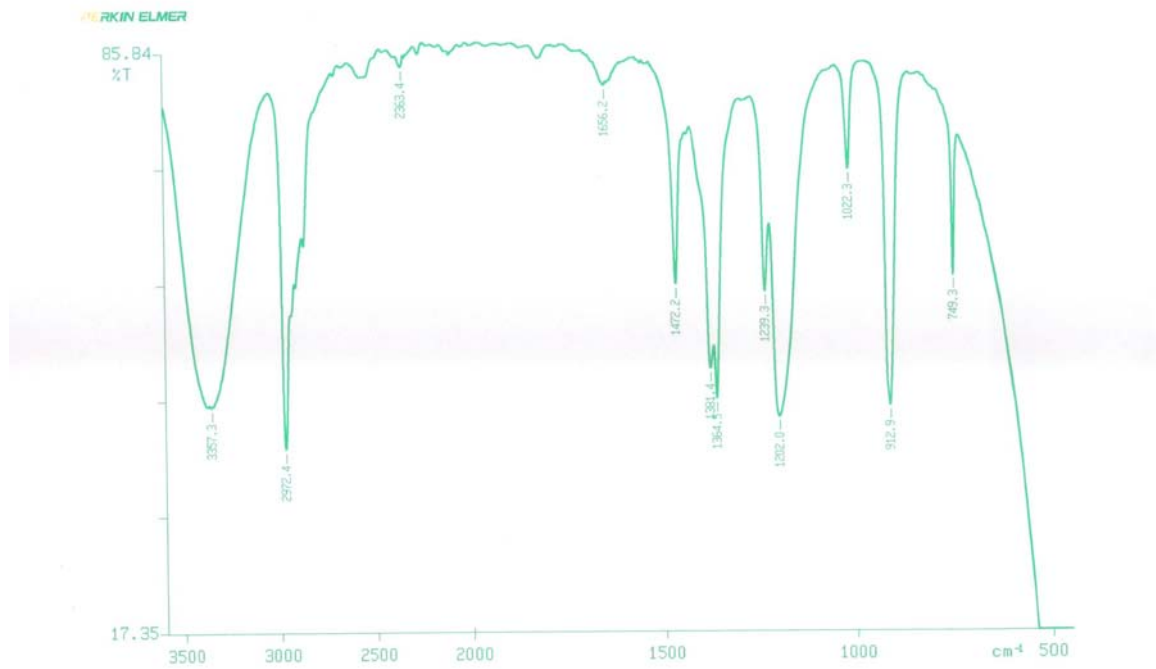
Problem 2 : Similar to the first problem, please try using unsaturation number and your knowledge of IR landscapes to propose a structure or structures that fit the following information.

C42H30



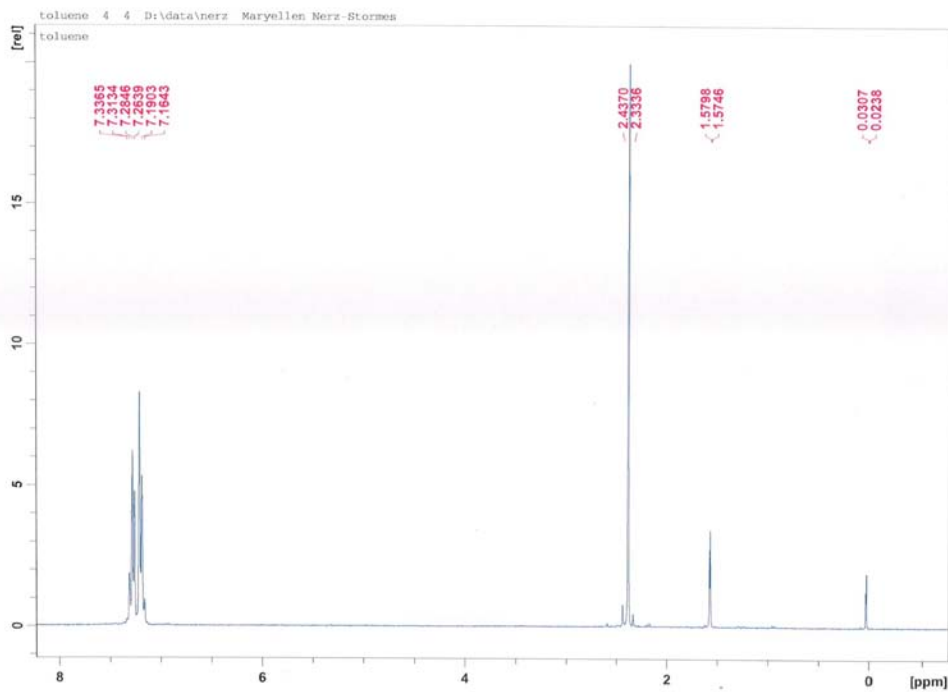
10/04/15 13:15 Peter hexaPhBenzene
X: 1 scan, 4.0cm⁻¹

Problem 3 C₄H₁₀O



10/03/26 11:25 rosoff-mohan-zinn
X: 1 scan, 4.0cm⁻¹

Problem 4 C₇H₈ with contamination (C₃H₆O) Draw structure of both the contaminant and the compound



Maybe give them this before we do problems. Problems will be having formula and trying to come up with reasonable structures.

Good website for general info about NMR/IR and functional groups.

<http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/nmr/nmr1.htm>

1. This webbook is dedicated to all my chemistry teachers, especially Dr. Edward R. Thornton and Dr. George Furst who taught me something about spectroscopy, to Dr. John Wasacz who interested me in spectroscopy and finally, to Dr. Kenneth Brumberger who patiently explained my radiology films to me over the years and developed my interest in radiology and my perception of it as being really spectroscopy. Of course, to my oncologist Steven Cohen who encouraged me as an early patient to read my films and who often brought me down stairs to go over my films. This inclusion gave me the courage to become a lampshade radiologist at home which helped me survive my cancer.

2. Bushong book.

3. Maybe my old favorite by koji nakaneshi