Organic chemistry – crib sheets

NMR and IR spectroscopy

Introduction to spectroscopy

Spectroscopy covers a range of techniques used to study compounds and how the different molecules interact with each other. All spectroscopy techniques (with the exception of chromatography) use an energy source to make the molecules do something which can be detected.

Nuclear Magnetic Resonance (NMR) works by making atoms act like small magnets which in turn alters a magnetic field.

Both ***infra red*** (IR) and ***ultra violet / visible*** (UV/VIS) work by exciting the molecule so that it absorbs light at a given frequency.

Mass Spectroscopy operates by exciting the sample into ions and then passing it through a high intensity electromagnetic field which will attract ions differently.

While spectroscopy will not necessarily give the final structure of a compound, it will give significant insight into the different environments each compound is in and from that an educated attempt at the structure can be performed.

NMR

Nuclear Magnetic Resonance is a technique which converts an atom into a “nuclear magnet” by placing it in a high powered electromagnetic field over a range of frequencies. The word “resonance” comes from the verb “to resonate” which means to move at a frequency individual to the substance (for example, a glass will resonate at one frequency while a piece of metal will resonate at another).

For an atom to have a nuclear magnet the atomic weight divided by the atomic number must not give a whole number (Carbon 13 [C^{13}] would give a nuclear magnet – 13/2 = 6.5, but C^{12} wouldn't – 12/2 = 6).

The sample under study is placed in a non-nuclear solvent (such as D_2O or DCl_4 – D = deuterium, an isotope of hydrogen) and then subjected to the high powered electromagnetic frequencies. At a particular frequency, the magnet will undergo a “spin flip” - it will go from the low to high energy state (Low energy would be having magnets with the N pole facing the S pole, high energy would be N pole facing N pole); the atom is said to be in it's “resonant state”. After the magnet has passed that, the atom “flips” back to the low energy state.

This flip is measured on a chart recorder

Chemical shift (δ)

The chemical shift is a relative measure of the amount of energy required for something to undergo a spin flip. It is measured relative to tetramethylsilane ($(CH_3)_4Si$ also known as TMS), TMS is always given a value of 0.

The shift is an easy to understand system – it is a relative system so frequencies and units aren't required.

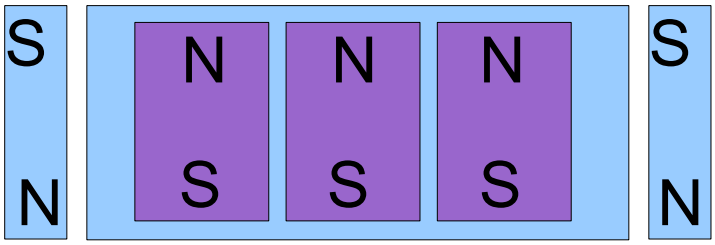
The shift gives a number of pieces of information about the compound, the most useful is what carbonyl groups are in there (for example, CH_3, $-CH_2-$, phenyl, carboxylic acid etc.). It also gives an idea on the amount of deshielding there is on a group.

Some groups “protect” the atom. This is known as shielding. When a group removes the protection (such as groups with electron withdrawing properties), it is known as “deshielding”. This moves the position of the compound further from the 0. This is known as being moved “up field” from 0.

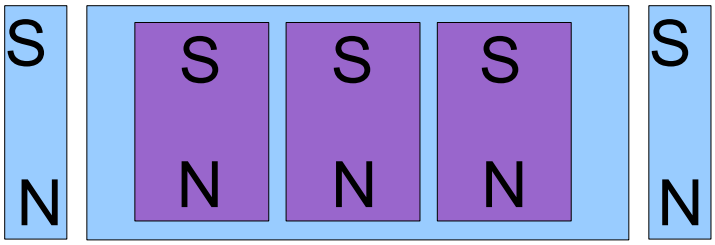
Fine resolution NMR

As previously said, when a nucleus flips at a frequency, it will go from the low to high energy state causing something to show on a graph. It will not though tell you much about the number of protons (a proton is another name for a hydrogen). This will be given on a fine resolution NMR spectrum (fine resolution is also known as high resolution).

To understand how a fine spectrum works, each hydrogen has to be thought of as being a magnet

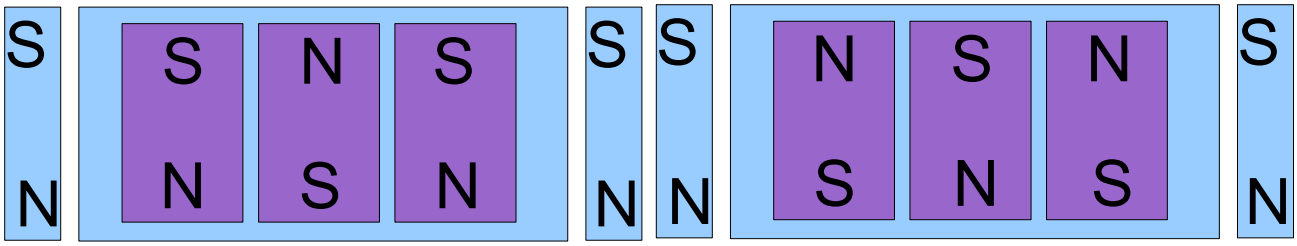


The sample here contains 3 protons. Each proton is lying opposite to the magnet. This would be considered to be a low energy state for each of the magnets. To excite the molecule, the frequency of the magnet is altered.



In this case, the induced field has caused all of the protons to flip against the direction of the field; they are now all in the high energy state.

However, two other states exist (below)



In these two final cases, two magnets are in the high energy state (left) and two magnets are in the low energy state (right).

This means that for a compound with 3 carbons, there are 4 possible states for the magnets.

This gives rise to something known as “spin splitting”. This is where protons affect the number of peaks on the neighbouring molecule using the *n+1* rule (*n* = number of protons.

A CH_3 has 3 protons so splits its neighbour into 4 peaks, the neighbour then splits the CH_3 into however many protons it has + 1 peaks – so a CH_2 would split a CH_3 to 3 peaks or a CH would split a CH_3 into 2 peaks. If there are no protons, then there is a single peak). It is this splitting which gives the ratio of protons on a carbonyl.

Physical environment.

The physical environment will change the shift and the number of peaks.

Take CH_4. CH_4 has 4 protons, each in the same chemical environment. If the protons are in the same environment, there is only a single peak. The peak will have a ratio of 4 (ratio is given as a peak height usually)

Take CH_3CH_3 (ethane). This time there are 6 protons on two carbons. Each proton is still in the same environment. On a trace, this will appear at around δ0.9. Each CH_3 group will split the neighbouring CH_3 group into 4 peaks.

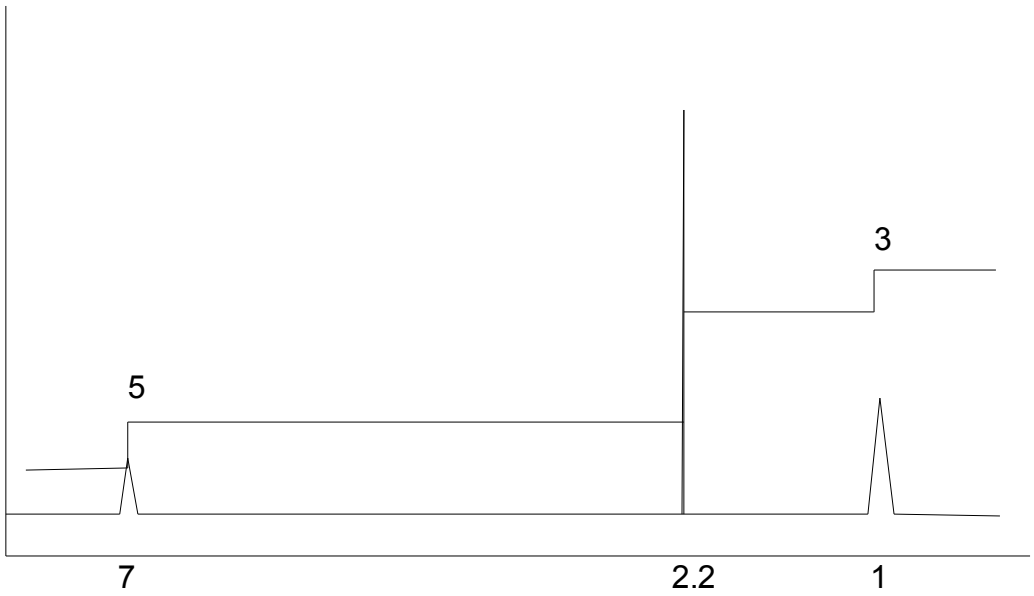
What about a ketone?

A ketone has a CH2 or CH3 group either side. As there are no hydrogens on the carbon with the oxygen bonded, there can be no splitting. As there are no hydrogens, there can be no splitting. Propanone will therefore just have one peak at around δ2.0. If the ketone is not propanone, splitting may occur (for example butanone with have a single peak at about δ2, but there will also be a quartet (4 peaks) at ≈ δ0.9 and a triplet (3 peaks) at about δ4)

Integration line

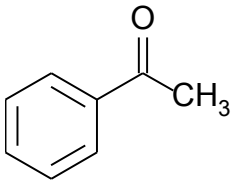
The beauty of NMR is that is gives the ratio of hydrogens as a value which helps in determining the number of hydrogens on any given carbonyl. The only problem is that this ratio has to be read off from a graph and then altered mathematically it give a value which makes sense.

The integration line is a line which directly tells the number of hydrogens on the carbonyl.



The diagram above gives a PMR scan of a compound. Note there are 3 peaks, but only 2

numbers given. This is due to the peak at 2.2 being a ketone. A peak at δ7 is that of a phenyl group with a single peak at δ1 being a CH_3 group. The number gives the number of hydrogens on the group. As there is no splitting of either the phenyl or the methyl groups, the ketone must be between them. If this information is all put together, it gives a final possible structure of



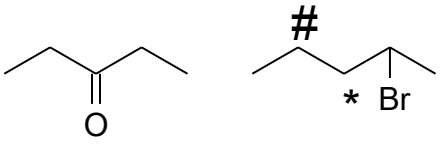
Understanding the integration line and splitting patterns

A common type of question regarding splitting is what splits what? Take CH_3-CH_2-CH_3. The CH_3 groups will split CH_2 into a quartet at about δ1.3 with the CH_2 splitting both of the CH_3 groups into a triplet at δ0.9. Without the integration line, it would be impossible (or at least very difficult) to give anything more that the compound having a CH_3 and CH_2. However, the integration would show 6 at δ0.9 and 2 at δ1.2.

It is impossible for a group to exist (a carbon cannot be left with an unbonded electron), therefore the structure can be easily found.

The shifting -CH_2- group

A -CH_2- group is given in most tables as being at around δ1.2. Unlike a -CH_3 though, the CH_2 can be anywhere in a chain and so the environment surrounding it will alter the position. Take the two molecules below



The CH_2 will move depending on the deshielding effect of the neighbouring group. For the ketone, the CH_2 groups will move to around δ3.4; the effect of the negative charge of the ketone pulls a positive charge to the carbon the double bond is on, this will pull the CH_2 upfield. It will still be split into a quartet by the CH_3.

There are two types of CH_2 group in the 2-bromopentane. The group next to the bromo group (marked with a *) will be pulled upfield due to the negative charge on the bromo group, however next to that is a second CH_2 group (marked with a #) which will pull back downfield so the CH_2 groups will appear closer to δ2.

In short, CH_2 can move as far upfield as δ4.2, so care needs to be taken when assigning groups!

Using the NMR look up table to assign peaks.

A look up table gives the “normal” value range(s) for where peaks can normally be found (such as δ0.9 for CH3 and δ6.5 – 8 for phenyl). This is known as an “indicative” value for a peak. To assign a peak, find the groups for that value.

This though is a problem – many groups can have similar values. Ketones and benzene are both in the same region (δ2.1 – 3) with bromo and iodo groups also in that region.

Seeing which group is present is made simpler with the integration line and splitting (a H-C-halide will split the neighbouring group into a doublet, benzene into a septet (7 peaks) and a ketone into a singlet (1 peak)).

A simpler method of determining which peak is which is to combine the NMR reading with another form of spectroscopy, IR.

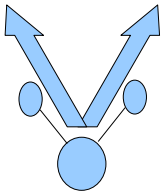
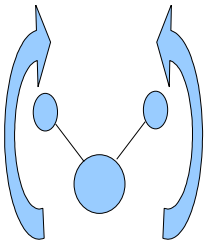
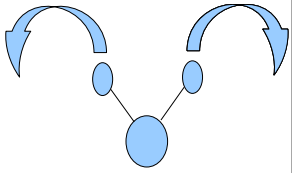
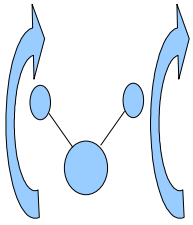
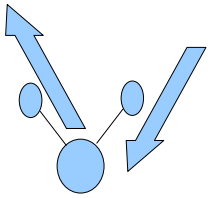
Infrared (IR) spectroscopy

IR works by hitting a molecule with infra red radiation. At a particular wavelength, the energy is absorbed which excites the molecule making it vibrate.

IR spectroscopy can be carried out in the gas phase (such as for CO, HCl and SO_2), liquid phase (simple organic compounds) and solid phase (plastics and rubbers). The action of a molecule in any of these states does not change if it is in liquid, gas or solid states.

Vibration types.

When a molecule vibrates it can do so in any of 5 different ways. On a detector, this is picked up as having had a different transmission (how much light is let through) – different vibrations (known as modes) absorb different amounts of light.

Mode	Name and example
	Symmetrical – arms move out opposite to each other : HBr and methane do this.
	Scissor – arms move in together. SO_2 in the gas phase
	Wagging – arms move forward and out opposite to each other. Typically seen in solids (rubber and latex)
	Waving – arms move left to right together. Certain organic solvents (typically symmetrical with a bridging molecule such as ethers)
	Unsymmetrical bending – one arm moves in as the other moves out. CO_2 in the gas phase

An IR Spectrum

Unlike other types of spectrum, an IR spectrum is a % transmission spectrum – it starts at the top and dips down when the light is not absorbed (100% transmission = 100% absorbed light). The x axis is measured in wavenumbers v (Greek letter nu. It has a value of 1/wavelength [1/λ] with a unit of cm^{-1})

The spectrum is split into a number of regions

Above ≈ 3200cm^{-1} is the -OH stretch region. If a carbonyl has an OH group (such as carboxylic acids or alcohols) the OH will absorb light in this area. It is normally quite a broad (thick) band, but doesn't have to be.

Between 1500 and 3200cm^{-1} is the carbonyl stretching area. As with NMR, there are a

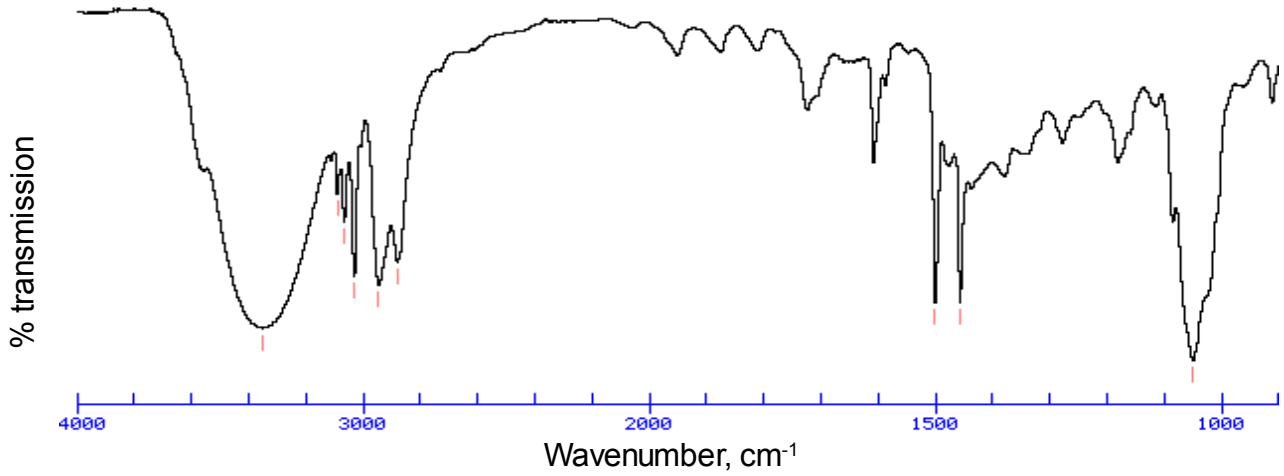
large number of carbonyl groups which overlap each other (such as ketones and aldehydes – they both have a C=O stretch). This makes absolute confirmation of an IR scan and the structure of the molecule difficult (which is why IR is normally combined with NMR – a ketone has a peak at δ2.2 while the aldehyde is at around δ9)

Between 1000 and 1500cm^{-1} is the fingerprint region. The fingerprint region aids in finding the position of groups (for example a primary alcohol with have a peak at around 1050cm-1 with a secondary being about 1100cm^{-1}. NMR cannot really tell you if an alcohol is 1º, 2º or 3º though it may be indicated by the amount of deshielding taking place).

Below 1000cm^{-1} is generally for the likes of C-halides and phenyl stretches (a stretch at ≈ 1450cm^{-1} and peaks between 690cm^{-1} and 900cm^{-1} would indicate substituted phenyl rings, again NMR peaks between δ6.5 to 8 would confirm it).

An IR scan.

An IR scan looks like this



The y axis shows how much light has been transmitted.

There are a number of different types of peak.

Broad and sharp peaks

Between 3200 and 3500cm^{-1}, the peak is described as being “broad” whereas the peaks at about 1500cm^{-1} are described as sharp.

Strong, medium and weak peaks

For both peaks, they are known as being “strong” as there is not a lot of light transmitted. The peak just above 3000cm^{-1} is a “medium” peak. Roughly 30% of the light is transmitted. The peak at 1700cm^{-1} is a “weak” peak. Some light is transmitted, but not a great deal (roughly 60%). It is rare ever to see 0% transmission.

As with NMR though, there are a number of carbonyls all with the peak values (for example, aldehydes, ketones and carboxylic acids are all seen at ≈ 1650cm^{-1} [due to the C=O stretch]. However, if there isn't a peak at ≈ 3200cm^{-1} [-OH stretch], it won't be the acid). This makes absolute identification difficult.

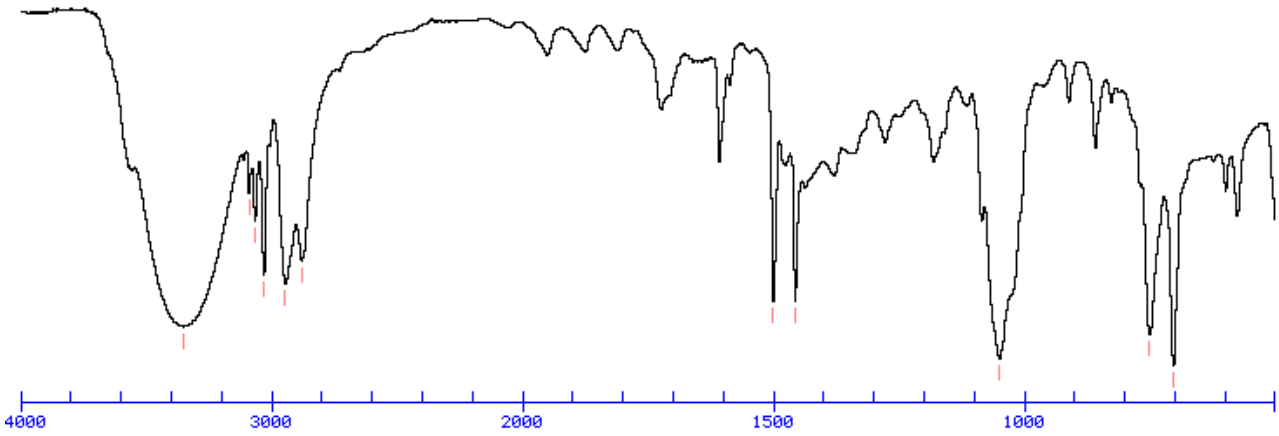
Using NMR and IR together.

An IR scan shows a peak at ≈ 1650cm-1. From a table, it was decided that this could be either an aldehyde or a ketone (the carboxylic acid option was ignored as there wasn't a stretch at ≈ 3200cm-1).

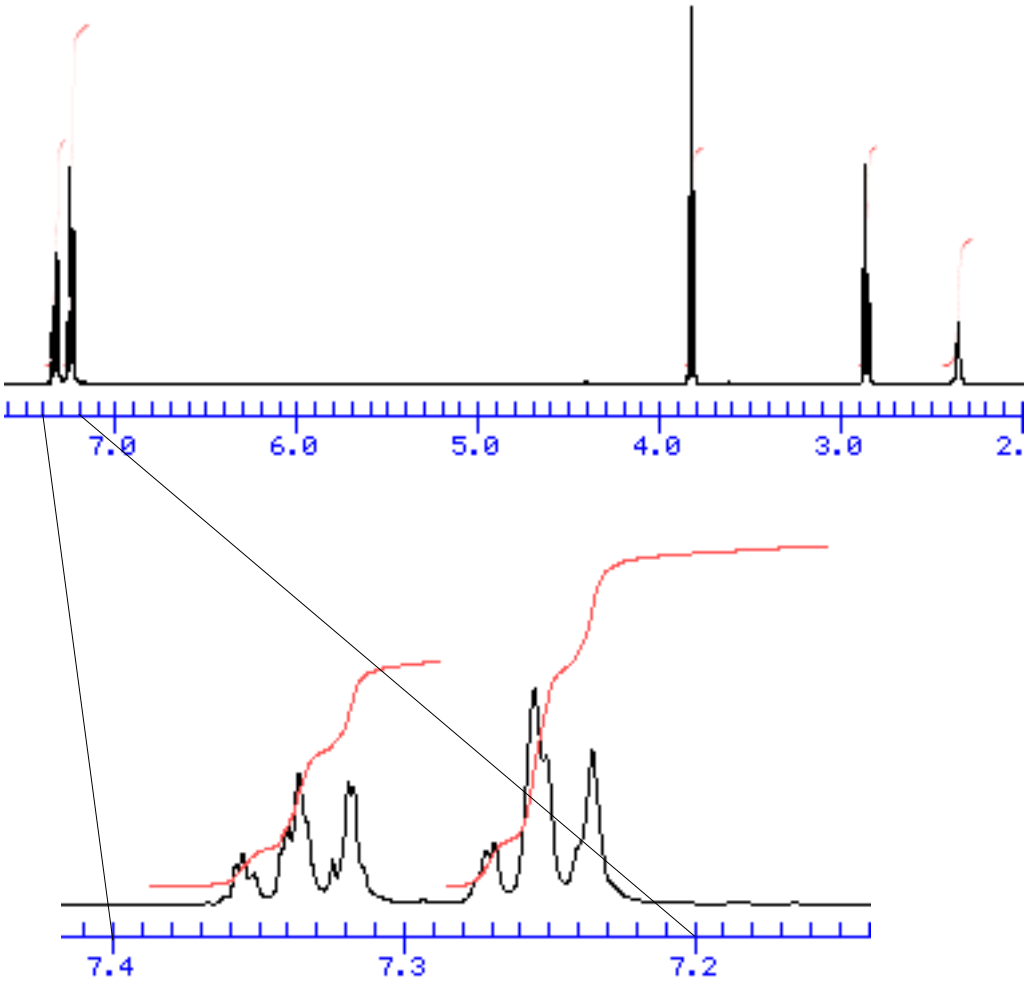
The NMR scan of the same sample as above did not show a peak at δ9 – δ10 (the peak associated with aldehydes). By this simple removal of options, the structure of compound can be found.

Example

IR Data



NMR Data



How can a compound be identified from these scans?

Take the IR and find all of the strongly absorbing (low transmission – the peak is near to the x axis) peaks and identify them

Peak value (cm^{-1})	Likely to be
3400	-OH (strong)
1500 & 1480	$-CH_2-$
1100	Possible ether, ester, primary alcohol, fluroalkanes
700 & 750	Mono-substituted benzene, ortho substituted, chloroalkane

Next look at the NMR scans

δ	Likely to be
7.2 – 7.4	Phenyl
3.8	CH2 (deshielded)
2.8	CH2
2.2	OH

What do both tables definitely show?

Both show a phenyl ring, both show an OH. Both show the phenyl ring and combined with the 700 and 750cm^{-1} peaks, it is a mono-substituted benzene (one H removed and replaced with a group)

As there is nothing on the NMR between δ4 and 4.5, there are no fluoroalkanes.

The ester can be discounted. The ester would show a peak at ≈ 1650cm-1 for a C=O stretch (same as would be seen for aldehydes and ketones).

While there are no numbers on integration lines for the peaks at 3.8 and 2.8, they are roughly double the size of the integration line of the peak at 2.2, suggesting double the number of hydrogens (remember, integration lines are proportional to the number of hydrogens on a group). This would suggest that there are two groups next to each other with the same number of hydrogens on. The peaks at 1500 and 1480cm^{-1} with NMR peaks at δ2.8 and 3.8 would be in agreement for $-CH_2-$

This would remove the chloroalkane (CHCl would have a different effect on CH_2 for the integration line) and ether (CH_2-O-CH_2 would cause a single line with no splitting at δ1.2)

Finally is the peak at δ2.2. While this is low for an alcohol, the IR shows a peak at 3400 cm^{-1} and 1100cm^{-1} (primary OH). There is a single H with an O in between the carbonyl and the H which would give a single peak (integration half of a CH_2).

Final structure