

Introduction to Spectroscopy VII: Approaches to Spectroscopy Problems

Introduction:

Spectroscopy problems in many ways are logic puzzles. Once you know the chemical shifts and wavenumbers of particular functional groups there really isn't much actual chemistry involved in solving the structures. Like all logic puzzles a rational approach helps a great deal in solving the structure. Listed below is a way of approaching spectroscopy problems. It is NOT the only way! Most people who do spectroscopy come up with their own favorite way of doing things so try things out until you come up with something that works for you.

A step-by-step approach:

- 1. Degrees of unsaturation a.k.a. double-bond equivalents.** This will give the *total number of rings and pi bonds*. It's not impossible to put together a structure if you don't have the formula, but it's orders of magnitude more difficult so the formula will nearly always be provided.
 - Each C gets 2 H plus 1 per end in a saturated molecule, so $(2 \times \#C) + 2 =$ hydrogen in a saturated molecule. Every nitrogen atom requires an extra H ($+\#N$), every halogen atom replaces an H ($-\#X$) and oxygen simply inserts and doesn't change the hydrogen count.
$$^{\circ}\text{Unsat.} = ((2 \times \#C) + 2 - \#H + \#N - \#X) / 2$$
 - If you have a ring this may be the only clue you have to its presence.
 - High degrees of unsaturation in a small molecule are a clue that a benzene ring (4 degrees of unsaturation) is present.
- 2. IR Spectrum.** Shows what *functional groups* are present.
 - Look at each of the 4 sections (X-H, triple bond, double bond and fingerprint) individually to determine what kinds of bonds are present.
 - Label each peak with what functional group it represents.
 - OH, alkyne H, and aldehyde H will show up distinctly.
 - C=O, and triple bonds show up here and may not show up clearly in the ^1H NMR as they tend to be quaternary carbons.
- 3. ^1H NMR Spectrum.** Shows *exact connections* and *functional groups* in the molecule. Working methodically so you don't skip any peaks (e.g. left to right) look at each peak and assign three things.

- a. Integration – How many H of that type.
 - i. Look for symmetry. There are no molecules (other than CH₄) where 4H, 6H, or 9H are equivalent unless you have two or more symmetrical CH₂ or CH₃.
 - ii. If your total number of H does not equal the number of H in the formula you likely have a symmetrical molecule.
 - b. Chemical Shift – What functional groups are nearby?
 - i. sp³ are to the right (0-5 ppm), sp² are to the left (5-10 ppm)
 - ii. Plain C-H are right most, then C-H next to a pi bond in the middle of the range, and then C-H next to an electronegative atom are to the left.
 - iii. OH and NH can hydrogen bond so vary a great deal in chemical shift, but will show up as broad singlets that never couple to neighboring H.
 - c. Coupling – How many nearest neighbors.
 - i. N+1 rule for all alkanes.
 - ii. Remember that no single neighboring carbon can have more than 3 attached H.
 - iii. Complex splitting around alkenes requires more work but follows the n+1 rule for each individual coupling.
 - a. Allyl and alkyl couplings can be d, t, or q.
 - b. Geminal and vicinal couplings can only be d.
4. **¹³C NMR Spectrum (118B/C).** Shows number of C. Useful for finding *quaternary carbons*.
- a. Esters (180-165 ppm) and ketones (210-195 ppm) are easily differentiated by ¹³C NMR, but not by IR or ¹H NMR.
 - b. Look for symmetrical peaks.
 - c. Check for any quaternary carbons that did not show up in the IR or that you missed in the IR (C=O, alkynes, CR₄).
5. **Check.** Make sure you have all the atoms. Check the pieces you found in the ¹H NMR spectrum and the IR. Make sure you have all the degrees of unsaturation accounted for.
- a. Missing C, O, and degree of unsaturation – likely a carbonyl, check the IR/¹³C NMR.
 - b. Missing 2C and 2 degrees of unsaturation – likely an internal alkyne, check the IR/¹³C NMR.
 - c. Missing H or extra H – you did the ¹H NMR wrong.
 - d. Missing just a C – likely a quaternary carbon check the ¹³C NMR
 - e. Missing degrees of unsaturation but no atoms – likely a ring.

6. **Put the puzzle together.** Use the information from step 3 to put pieces together. Many molecules have 'handles' where you can get started, places where there really is only one CH group that can attach at that particular position. What works for one molecule will not necessarily work for others, but places that can be helpful to start are:
- a. *Ends vs. Middles:* Keep track of what pieces are ends (only 1 missing attachment) and which are middles (more than 1 missing attachment). You can't attach two ends together unless they are the last two groups in the molecule or you won't have anywhere to put the rest of the pieces.
 - b. *Coupling:* Look at your coupling and join pieces by how many neighbors are needed to get the correct coupling.
 - i. Often there will be only 1 CH or CH₃ or CH₂, where does it attach?
 - ii. Chains of CH₂ will tend to have two CH₂ with two neighbors (ends) and one or more CH₂ with four neighbors (middles).
 - iii. A 6H doublet is always two CH₃ attached to a CH (isopropyl) look for the CH with many neighbors and figure out how many neighbors are unaccounted for.
 - iv. No coupling often means no neighbors.
 - c. *Electron-withdrawing groups:* What CH is next to a pi bond? What CH is next to an O or N or X?
 - i. Placing an OH, or C=O can limit where else you can put pieces and make middles into ends.
 - ii. Differentiating between groups adjacent to pi bonds is difficult to do by chemical shift, consider the coupling as well.
 - iii. Alcohols and ethers need to have two groups attached to the oxygen, make sure you can find both of them. If only one is obvious it may be attached to a quaternary carbon.
 - d. *Symmetry:*
 - i. Are there symmetrical CH₂ or CH₃ (4H, 6H or 9H peaks)?
 - ii. Are all the H in the formula accounted for in the ¹H spectrum or are all the peaks doubled (or tripled)?
 - e. ¹³C NMR: Identify quaternary carbons.
 - i. Esters vs. ketones can only be easily seen by ¹³C NMR
 - ii. Symmetry can be confirmed by number of C peaks.
 - f. Once you've attached a few pieces go back and try the tricks that didn't work again, often eliminating a few pieces forces the rest to a particular position.

7. CHECK!!!!

- a. Make sure everything makes sense. Often something that seems out of place or strange will make sense in the context of the whole molecule – “Oh it’s downfield because it’s next to two different pi bonds...”
- b. If you’re sure of your assignments in step 2-4 DO NOT CHANGE THEM. It’s very common for students to ‘know’ that they have a CH_2 with two neighbors attached to an OH and instead they draw it as a CH or adjacent to a CH or $\text{C}=\text{O}$ just to make something else fit. If you change what you know is right to make it fit, the whole molecule is likely wrong. Start over instead.
- c. Every peak will be accounted for in the final molecule.
- d. Watch out for random hanging $-\text{CH}_2$ and 5 bonds to C.

Tips/Tricks:

- Know the chemical shifts in Tables 10.2 and 10.6 in Vollhardt+Schore and the wavenumbers in table 11.4. Without these doing spectroscopy problems is nearly impossible.
- Many times information about a functional group is available in several places. If you can’t remember a chemical shift, check the IR for the same group.
- Every time we cover a new functional group add it’s particular tricks to your process. Ask is this an alcohol or a phenol (chemical shift)? Ask is this an ester or a ketone and an ether (carbon chemical shift)?
- Find a way to indicate neighbors without writing the extra atoms. E.g. If you know something has two neighbors write -2- rather than CH_2 or you’ll often get extra atoms in your structure and not know which are real and which are placeholders.
- Everything will make sense in a correct molecule. If one of your pieces doesn’t fit, start over.
- If you’re confident that all your molecule pieces are correct, don’t change them just to attach them to a structure, likely the structure you’re putting together is incorrect.
- Practice practice practice. Like any logic puzzle the more you do, the easier it is to see the patterns and to recognize various common tricks.

Further Readings and References:

Silverstein, Robert M.; Webster, Francis X.; Spectroscopic Identification of Organic Compounds; 6th Ed.; John Wiley & Sons, Inc.; New York; 1998

Vollhardt, Peter; Schore, Neil; Organic Chemistry: Structure and Function; 6th Ed.; W. H. Freeman and Co.; New York; 2011

Pretsch, Ernö; Bühlmann, Phillipe; Badertsher, Martin; Structure Determination of Organic Compounds: Tables of Spectral Data; 4th Ed.; Springer-Verlag; Berlin; 2009

Wikipedia.com – IR Spectroscopy; NMR Spectroscopy; Mass Spectrometry and Ultraviolet-Visible Spectroscopy