Example NMR Analysis 1

Transcript

Instructor: Brett McCollum

00:00:00:40 - 00:00:32:05
Instructor: Now we're ready for a slightly more challenging example. Don't worry if you're finding it frustrating as you work through NMR. This is normal. Everyone feels frustrated as they start learning how to solve these types of problems. Keep at it because it might just take you another week or two with sufficient practice to start to see the patterns and be able to look at a spectrum and immediately start to recognize what information is available to you.

00:00:32:05 - 00:00:54:10
Instructor: I hope that you, like me, are soon going to find that these are fun. These are really enjoyable to solve. Let's get into this one together. We've been given our chemical formula. We have our NMR spectrum, and we have signals ranging from slightly above 2 PPM all the way up to around 11 PPM.

00:00:54:10 - 00:01:28:01
Instructor: That we haven't seen before. Let's build our table, so we can begin organizing the information captured in the spectrum. We now have our table complete. We recognize that we were told in our spectrum that A and C are triplets. The B and D, therefore, you can see our singlets.

00:01:28:01 - 00:01:48:05
Instructor: We looked at our integration of two to one to two to one. That adds up to six protons which matches our chemical formula. We know we've detected all of the protons present. There is no mirror plane here that would double any of these protons. We see them exactly as they are.

00:01:48:05 - 00:02:17:67
Instructor: Now we're ready to start putting our pieces together. So, let's start off by determining the degree of unsaturation so that we know how many rings or double bonds might be present in the molecule. We can put our degree of unsaturation. We know is two

times the number of carbons plus two, two times three plus two more is eight, subtract the number of hydrogens. There are no nitrogens or halogens present.

00:02:17:67 - 00:02:54:51
Instructor: We divide by two, and we get a degree of unsaturation of one. There is one double bond or there is one ring present in our molecule. I look at this, and the first thing that stands out to me is a signal over here at D. That's really high around 11 PPM. For an organic molecule, go look at your table, your spec reference table, and see if you can figure out what group must be present to represent signal D. Hopefully,

00:02:54:51 - 00:03:19:24
Instructor: you agree with me that there's only one option for signal D, and that is carboxylic acid. Carboxylic acid signals can range from about six to 13 PPM. This one is showing in that region up at 11. There isn't another option. Now, the great thing about this is we've found that double bond.

00:03:19:24 - 00:03:57:60
Instructor: There's only one degree of unsaturation in this compound, and it is present in the carboxylic acid. This proton right here is responsible for that signal. Now it's going to have another bond to it to the rest of the molecule. Let's go look at signals ABC if we can figure out their connectivity. We've figured out D, A and C have two protons present, that makes me think of a CH2 group and B has a single proton present, probably a CH.

00:03:57:60 - 00:04:47:66
Instructor: Thinking about our multiplicity, A being a CH2 group, that will have two bonds to it and because it's a triplet, it's going to have two neighboring protons. That could be a CH and a CH or a CH2. Now, it can't be directly attached to this proton because that one's on the oxygen of the carboxylic acid. There's only one other CH present, so it can't be two separate CHs. That tells us that signal A must be next to another CH2 group.

00:04:47:66 - 00:05:07:11
Instructor: Where is that other CH2 group? It's signal C. A and C are joined to each other. And we have that the signal C here. We also have two bonds to it.

00:05:07:39 - 00:05:33:43
Instructor: It is a triplet. It's having two neighboring protons. Since we know that A is next to C, C is therefore next to A. There's something else attached to C that fills the octet of that carbon. We've got a good sense of where A and C are in terms of their relationship to each other.

00:05:33:43 - 00:05:59:65
Instructor: We haven't explained why they're at such a high chemical shift because a CH2 group would normally show up at about 1.2 PPM. There must be something that is deshielding it. Well, we know one such group, that's the carboxylic acid, and that's going to be deshielding things. But we have some additional atoms in the molecule we haven't accounted for.

00:05:59:65 - 00:06:41:76
Instructor: For example, we know there are three oxygens and we've only used two of them for the carboxylic acid. We're thinking about what B might be, and while it's showing up as an integration of one and that could be a CH group, we then paused and we were thinking about our chemical formula. We only have three carbons present. We've used one in the carboxylic acid, one for the carbon of the CH2 group responsible for signal A, and we've used the last one for the carbon of the CH2 group responsible for signal C. There are no carbons left.

00:06:41:91 - 00:07:30:87
Instructor: The only other atom available to us in the chemical formula is that remaining oxygen. We know that signal B is going to be an OH group, which only needs one bond to complete the octet on this oxygen because of its lone pairs. That's going to be attached somewhere in the molecule. We've got our pieces, we just have to figure out how to fit them together, and it should explain our multiplicity as well as our chemical shift. So let's start off by saying we have a carboxylic acid on one end of the molecule. Let's draw that.

00:07:30:87 - 00:07:55:02
Instructor: OH bonded to a carbon that is double bonded to an oxygen, and that will be bonded to what? Because if we look here, we said there are three carbons, one, two, and three. There should be six hydrogens. One, two, three, four, five, six, and three oxygens, one, two, and three. We've found every atom here.

00:07:55:02 - 00:08:16:70
Instructor: Every piece as we fit it together is already on the board. We've got our carboxylic acid, if we attach that directly to the alcohol, that ends the molecule. There's only one bond permitted to that. That can't go here. It must be either A or C, both of which are a CH2 group.

00:08:16:70 - 00:08:38:23
Instructor: And then whichever one it is, is bonded to a CH2 group, which is bonded to something else. The only thing left is the alcohol. There we go. We've figured out what our unknown compound is. Now, let's see if we can take it one step further.

00:08:38:23 - 00:09:05:14
Instructor: We know that this, or really we should say, this is signal D. We know over here is signal B that the alcohol group can range between 0.5 and 5 PPM, showing up at 3.8, that works. But why is it a single?

00:09:05:14 - 00:09:56:23
Instructor: It has two neighboring protons. Shouldn't that be split? In fact, alcohols in a solvent that allows rapid exchange of that proton and an acid base reaction will not demonstrate spin coupling with the neighboring protons. The alcohol will show up as a singlet, and then those neighboring protons in turn, they don't couple with the alcohol, and so they will not experience any splitting due to it, only due to other neighbors. That's why

this CH2 is showing up as a triplet, not having additional splitting to a quartet or some other option due to that alcohol.

00:09:56:55 - 00:10:32:68
Instructor: We found what is signals B and D. Can we differentiate between A and C based on their chemical shift? But we have to think about what is the amount of chemical shift that occurs as a result of being near a carboxylic acid versus being near an alcohol. Check your data table and you should see that if you are near the carboxylic acid double bond, this should be around 2.2 to about 2.7 PPM.

00:10:32:68 - 00:10:49:06
Instructor: It could be as low as 2.0 if it was a CH3 group, given that it's a CH2, I'm going to expect it's going to be in the middle of 2.0 to 2.7 at about 2.4 PPM.

00:10:49:06 - 00:11:12:26
Instructor: What does that match on our table? Right there. This is signal A. Then the CH2 group next to an alcohol. That's going to be further deshielded, and we expect that that would be around 3.3 to 3.6 PPM.

00:11:12:26 - 00:11:23:70
Instructor: Since this is CH2, CH3 is 3.3, the CH is 3.6, somewhere in the middle. I'm going to expect it to be around 3.5 PPM.

00:11:23:70 - 00:11:55:77
Instructor: It's showing up a little bit higher. That's okay, though. That could be due to additional electron withdrawing effects of that carboxylic acid, that we have some inductive effect with drawing electron density further deshielding signal C in our spectrum. We've been able to determine what each of our signals corresponds to within our molecule. You're now ready for some more challenging problems.

00:11:55:77 - 00:11:58:29
Instructor: Go ahead and keep working.