Interpretative Spectroscopy

Prof. Maravanji S. Balakrishna

Department of Chemistry

Indian Institute of Technology Bombay

Lecture 52

Problems and Solutions-2

Hello everyone. Once again, I welcome you all to MSB lecture series on interpretative spectroscopy. So, we really started looking to the problems to make ourselves more familiar with interpretation of the data obtained from these important force spectral methods. This helps in understanding what if we are familiar with interpretation it would be very easy to elucidate the structure and also look into the properties and reactivity and also applications in many avenues. So, let us solve more problems in this lecture as well. Let us look into one problem here.

11. The following peaks were from a ^{1}H NMR spectrrum from a 300 megahertz (MHz) spectrometer. Convert to PPM unit.

One is 693 hertz and another one is 1060 hertz.

Again we know the instrument frequency and simply divide chemical shift in hertz by the spectrometer frequency you get in PPM.

693 divided by 300 into 10 raise to 6 ($\frac{693}{300\times10^6}$) would give you 2.31 into 10 to the power minus 6 (2.31×10^{-6}) or 2.31PPM and

Similarly, the second one this one becomes 3.53 PPM.

For example: In a ^{1}H NMR spectrum recorded at 300 megahertz CHOH appears at 2.31, whereas CHCl appears at 3.53 PPM and you should remember this chemical shift value in PPM does not change with the field strength. Whether you take 500, 600, 700 it still remains 2.31 only. The corresponding chemical shift in hertz increases but once when you take the ratio it is independent.

That is the reason we represent always chemical shift in PPM to avoid any confusion and minimize complexity.

12. Butane-2-one shows a chemical shift around 2.1 PPM on a 300 megahertz (MHz) spectrometer in the ^{1}H NMR spectrum.

i) How far down field is this peak from TMS in hertz (Hz)? TMS always at 0.

ii) If the spectrum was done with a 400 MHz instrument, would a different chemical shift be seen

iii) on 400 MHz spectrum, what would be the difference in hertz (Hz) from chemical shift and TMS?

Three questions are there associated with this question.

First one is how far down field is this peak from TMS in hertz? For that, what one should do is multiply 2.1 by 300 into 10 raise to 6 and divided by 10 raise to 6 ($\frac{2.1\times300\times10^6}{10^6}$), which will give 630 hertz. So, the peak at 2.1 PPM would show at 630 hertz on a 300 megahertz (MHz)spectrometer.

We converted from PPM to hertz, since TMS is always at 0 Hz, so the peak would be 630 Hz down field from the TMS.

If the spectrum was done with a 400 MHz instrument, would a different chemical shift be seen? The answer is no. A different chemical shift cannot be seen in PPM. The objective of using the PPM scale is make chemical shift independent of magnetic field strength.

And then on 400 MHz what would happen? Simply multiply a 2.1 PPM with 400 (2.1 x 400) so then you get 840 Hz. That means on a 400 MHz, chemical shift will be appearing at 840 Hz and again if 840 Hz if you divide by 400 ($\frac{840}{400}$) you get by your 2.1. So, this itself shows how chemical shift measured in PPM is independent of magnetic field strength.

Now let us look into another example focusing on ^{1}H NMR or NMR spectroscopy.

13. If you look at a spectrum of para-xylene or 1,4-dimethyl benzene (is called paraxylene), how many types of protons are there and what does the ratio mean?

Two signals as there are two types of hydrogens, the ratio is 1 to 1.5. The area under the peak at 2.19 ppm is 1.5 times greater than the area under the peak at 7.0 ppm. This molecule has two sets of protons: the six methyl (H) protons and the four aromatic (H) protons, the ratio is 1:1.5.

I have taken ^{1}H NMR for 1,4-dimethyl benzene, which is shown here. We have two signals, both are singlets. Singlet one can readily identify for methyl group and this one is for aromatic hydrogen atoms. If you look into the ratio, with integration, it is for 6 protons and it is for 4 protons and then the ratio will be 3 by 2 (3/2), i.e. 1 is to 1.5 (1:1.5).

It is interesting now to know how many different types of carbon atoms are there in this molecule. We have three different types of carbon atoms which can be seen in the ^{13}C NMR spectrum shown here at 21.3 (2), 128.9(4) and 135.4(2).

14. Predict how many signals the following molecule would have and the integrations in ^{1}H NMR? Sketch the spectra and estimate the integration of the peaks.

If you just look into the molecule, you can clearly tell that three types of signals are anticipated in ^{1}H NMR for this molecule. Also, if you look into ^{13}C, it should show 3 type of signals as all 3 are different. The CH_2 is split by this one to give a quartet. This will give a triplet and this will give a singlet.

Dibromo compound also shows two different types of hydrogen atoms. These two are identical show a triplet and then this will be coupled with these two show a triplet. So, we can anticipate two triplets here. Similarly, its ^{13}C NMR spectrum also shows two peaks, at 40.3 and 54.9 ppm.

15. How many proton signals are expected in the ^{1}H NMR spectrum of the compound shown below? Also predict the number of ^{13}C NMR signals.

If you just look into it this looks like a very symmetrical molecule. You can do C_2 rotation; both the portions on left and right bridged by methylene look identical and these two are identical and then this one and this one are identical. This one with no hydrogen and these two are identical and these two are identical. That means basically 1, 2, 3, 4 signals are expected, in its ^{1}H NMR spectrum. In ^{13}C NMR, if you see this is 1 this is 2 this is 3 this is 4 this is 5, this is 6 and this is 7. A total of seven signals are expected.

I have shown here values at 3.96, 6.90, 6.95. 7.14 and then at 9.58 for OH.

16. Solve the structure using the following spectral data. Molecular formula is $C_6H_{12}O_3$ IR spectrum is shown below.

I have also taken ^{1}HNMR spectrum.

You should notice here a carbonyl peak in IR. Then you have CH and then of course you have OH is also there so that means these things we have identified. We have 1, 2, 3, 4, 5, 6, 6 signals. If you see the spectra provided here, everything is clearly analyzed and appropriate signals are shown here in the slide.

I think let me stop here and continue discussion on some more interesting examples in my next few lectures. Until then have an excellent time. Thank you.