

Interpretative Spectroscopy
Prof. Maravanji S. Balakrishna
Department of Chemistry
Indian Institute of Technology Bombay
Lecture 51
Problems and Solutions-1

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. You must be very happy now because I will be solving from here onwards problems. One thing you should remember, when we are learning science subjects and if we learn those subjects through problem and those subjects are not a problem at all. For example, chemistry is not a problem if it is learned through problems. Mathematics is full of mathematics, full of problems and if we solve problems understanding the mathematical logic would be very easy. Similarly, physics is full of problems and if we learn physics through problems and physics is not a problem.

Similarly, if you learn spectroscopy through problems using our basics it is not a problem. It is enjoyable. So, let us start solving the problems. The next 8 to 9 lectures I will be focusing on solving very different type of problems having data from all these spectroscopy methods that I had discussed in my last 50 lectures or so.

Let me begin with some simple questions, simple problems and then go on to little bit more complex problems. Let us look into mass spectrometry related problem here.

The question is: what are the masses of the charged fragments produced in the following cleavage pathways. Two reactions are there. What you have to do is identifying the masses of the charged fragments produced in the following pathways and also what kind of fragmentation happens is also given here.

The first one is alpha-cleavage (α -cleavage) of triethylamine. The second one is McLafferty rearrangement of 4-methyl-2-pentanone.

Let us look into one at a time. In order to know about the fragment and its mass we should know the reaction. For example, what is the molecule we are considering and what kind of breakage happens and when the breakage happens what kind of fragments comes out.

So, let us begin first with alpha-cleavage (α -cleavage) of triethylamine(Et_3N).

Let me write, here, we have a lone pair. To have a better picture of cleavage, I am expanded something like this.

Now the cleavage occurs here. Of course, we are considering a radical cation. It proceeds through alpha-cleavage(α -cleavage). What we get is this one here. So if you just look into this one, 1, 2, 3, 4, 5 are there. $\text{C}_5\text{H}_{12}\text{N}$. And if you look into m by z (m/z) value will be 86.

So that means 60 plus 12 plus 14, 86($60+12+14 = 86$). So this is the one they have asked for.

What are the m/z values of fragments? In case of alpha-cleavage of triethylamine it is 86.

Now let us look into the second one, 4 methyl 2 pentanone.

Now for convenience of showing this rearrangement, I would write in a little different way. Of course, this is where it is going to fragment. Once we know that one the job is done. For this molecular weight is 100 and this one is $\text{C}_6\text{H}_{12}\text{O}$. So this would give this rearrangement.

So, this portion I am writing here. Just look here this is $\text{C}_3\text{H}_6\text{O}$, this is 58 and then this one is m/z equal to thirty six plus six is equals to forty two ($36+6=42$). So, this is what the question is asking.

Let us go to another very simple problem. What is the frequency of a wave with a wavelength of 200 centimeters?

Of course, we are familiar with energy; how it is related to frequency. E equal to $h\nu$ and equal to C by λ ($\nu = c/\lambda$), where C is the velocity of light. It is 3×10^{10} centimeters per second (3×10^{10} cm/sec) or 3×10^8 meters per second (3×10^8 m/sec).

We can use here and 200 centimeter is the wavelength given. If you calculate, what we get is: 1.5×10^8 hertz (1.5×10^8 Hz). This is the answer, very simple here.

Now another one: A radio transmits a frequency of 100 hertz. What is the wavelength of this?

one again you can use the same analogy here.

Here 100 is given. equal to 100 hertz is given. We have to calculate the wavelength. So, equal to C by λ ($\nu = c/\lambda$). In the same way λ equal to C by ν ($\lambda = c/\nu$). This corresponds to 3×10^{10} divided by 100 ($3 \times 10^{10}/100$).

It gives in centimeters and it can be converted into 3×10^6 meters (3×10^6).

4. Now without calculations simply by reading you should be able to answer: Which molecule 2,5-heptadiene or 2,4-heptadiene would you predict to have a lower heat of hydrogenation.

2,4-Heptadiene is expected to have a lower heat of hydrogenation than 2,5-heptadiene. This is due to the conjugation between the double bonds in 2,4-heptadiene, which is stabilizing.

5. What is the energy range for 400 nanometer and 500 nanometer in the UV spectrum where a compound absorbs.

So here again we should use $E = h\nu$

we have to calculate the energy associated with 400 nanometer as well as 500 nanometer radiation. So we should use E equal to $h\nu$ ($E = h\nu$).

If you simplify this one what it gives is 4.965 into 10 raised to minus 19 joule (4.965×10^{-19} J).

So what we have done is everything is given in meter for example, velocity of light is three into 10 raise to 10 centimeters (3×10^{10} cm) that should be made into 3 into 10 raise to 8 (3×10^8 m). Here also we have made it 10 raise to 7 (10^7) and then if you just take this one to numerator, we get this value. So this is the one for 400 how good 500 in the same way we can do it. So, this will give you value 3.972 into 10 raise to minus 19 (3.972×10^{-19}) to 4.965 into 10 raise to minus 19 Joule (4.965×10^{-19} J).

So this is the range that is asked in this question.

6. which one would absorb a longer wavelength: 1,3-cyclohexadiene or 1,4-cyclohexadiene. Similar question I had discussed about heptadiene.

1,3-cyclohexadiene would absorb a longer wavelength. More conjugation in the molecule, longer the wavelength absorbed.

7. Where is radio frequency radiation on the energy scale of the electromagnetic spectrum.

RF radiation includes radio waves and microwaves, is at the low energy end of the electromagnetic spectrum. It is a type of non-ionizing radiation

This information you should know. In the beginning I showed you the electromagnetic spectrum starting from UV to the higher energy or lower wavelength to higher wavelength.

Try to be familiar with those things, so that you know UV visible x-ray all ranges and where exactly the energy range falls in that electromagnetic radiation spectrum.

8. Now there is a question: ^1H requires 200 megahertz (MHz) of energy to maintain resonance in a magnetic field of 4.7 Tesla. If atom X requires 150 megahertz (MHz), calculate the amount of energy required to flip the nuclear spin of X. Is it greater than energy required for hydrogen?

That means ^1H nucleus requires 200 megahertz of energy to undergo nuclear transition in a magnetic field of 4.7 tesla and if atom X requires 150 megahertz, how much energy is needed for this X nuclei to undergo nuclear transition? That is the question. That means is it greater than the energy required for hydrogen? One has to calculate.

Simply we should use the equation $E = h\nu$. h value we know and then this value is given for $\nu = 150$ megahertz.

This will come around 9.93×10^{-26} (Joule). This is equal to 9.93×10^{-26} Joule.

Similarly, we can calculate for hydrogen, which is 1.324×10^{-26} Joules. The value is smaller here compared to that of hydrogen.

9. Calculate the energy required to flip the spin of a nucleus at 400 megahertz. How about the changing the frequency to 500 and 300 MHz.

We should calculate energy required to perform transition of a spin at 400 megahertz and then we have to see what would happen if we use frequency of 500 or 300 megahertz. Let us calculate for 400 megahertz; what we get is 2.648×10^{-25} Joules.

For 500, it is 3.310×10^{-25} Joules. For 300 megahertz, 1.986×10^{-25} joules. That means for 500 MHz, energy increases, for 300 relative to 400 energy decreases. So, this we know, if you recall, as magnetic field strength increases the energy gap increases.

10. For CHCl_3 , chloroform there is a peak at 2904 hertz in a ^1H NMR spectra taken from a 400 megahertz spectrometer. Convert this value to ppm.

How to calculate? Chemical shift in ppm is equal to frequency divided by spectrometer frequency. Here, 2904 divided by 400 megahertz (2904/400 MHz) will give in ppm. The value is 7.26 by 10 raise to 6 (7.26×10^6) means it is 7.26 ppm (parts per million).

If you look into ^1H NMR spectrum of chloroform, it shows a sharp peak at 7.26 ppm.

This is how we can convert chemical shift in Hz into ppm. Why we represent chemical shift in ppm? Chemical shift in ppm is independent of field strength. That also we shall look in some problems in my next lecture until then have an excellent time reading and solving more problems on spectroscopy to make yourself familiar with interpretation, characterization and elucidation of structures of new molecules. Thank you. .