

Interpretative Spectroscopy
Prof. Maravanji S. Balakrishna
Department of Chemistry
Indian Institute of Technology Bombay
Lecture 33
Hook's Law- Numericals

Hello everyone, I once again welcome you all to MSB lecture series on interpretative spectroscopy. I hope you are all doing very well, if so, let me continue from where I had stopped about discussing on infrared spectroscopy. In my previous lectures, I was telling about how the stretching frequency of a diatomic molecule or of a bond can be related to its reduced mass and also the stretching force constant. The simplest equation one can think of is nu bar ($\bar{\nu}$) equal to 130.3 into square root of F over mu (μ) ($\bar{\nu} = 130.3\sqrt{\frac{f}{\mu}}$) and in some equations for stretching force constant K is also used as an abbreviation, does not matter, whether F or K, you should remember, this refers to stretching force constant and where F is stretching force constant and mu (μ) is the reduced mass and reduced mass can be easily calculated by taking ratio of m1 into m2 divided by m1 plus m2 ($\frac{m_1 m_2}{m_1 + m_2}$) and this equation is the simplest one, and when we are using this equation what you should remember is, reduced mass is given in atomic mass unit and then force constant is given in newtons per meter (Nm^{-1}) and frequency in centimeter minus (cm^{-1}), you should remember that one.

Apart from this simpler equation, nu bar ($\bar{\nu}$) equal to 130.3 into square root of F over mu (μ) ($\bar{\nu} = 130.3\sqrt{\frac{f}{\mu}}$). We have a couple of more equations. one is, I have shown here, of course, this is from this one. Both the equations are derived here: nu bar ($\bar{\nu}$) equal to 1 over 2 pi c into square root of F by mu (μ) ($\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}}$) and if you simplify this one, it leads to mu bar ($\bar{\nu}$) equal to 4.12 into square root of F over mu ($\bar{\nu} = 4.12\sqrt{\frac{f}{\mu}}$) and only thing is little bit variation will be there as far as the units of force constant are concerned. Let me tell you, how this is derived and that is simplified into this equation here. The Hooke's law

expression can be simply transferred into a very useful and simple or simplified equation in this manner. We know that $\bar{\nu}$ equal to $\frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$. This comes again by ν equal to $\frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ by μ ($\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$). This comes again by ν equal to $\frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ by μ ($\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$); but ν equal to $\bar{\nu}$ by c ($\nu = \bar{\nu}/C$). Therefore, what we do is, we are simply putting this value here, and then this is what we get here. Then μ equal to $\frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass and $\bar{\nu}$ is frequency in centimeter minus 1 (cm^{-1}) and c is velocity of light 3×10^{10} centimeter per second (3×10^{10} cm/sec) and K is force constant in dynes per centimeter (dynes/cm).

That means in this one, the force constant is given in dynes per centimeter (dynes/cm), but in the simplified one, where I showed it is $130.3 \sqrt{\frac{F}{\mu}}$ (where we are considering the force constant in terms of Newtons per meter (N/m). That conversion fact has to be added here, if you want to use this equation and again μ equal to $m_1 m_2$ and then we are also adding to denominator Avogadro number and then this will give masses of atoms in amu and then if we simplify further by adding Avogadro number from the denominator of reduced mass expression and taking the square root, we obtain this simplified equation here. If we apply here, add the constants such as π (22 by 7) and c 3×10^{10} , it would simplify to this format here. So, $4.12 \sqrt{\frac{k}{\mu}}$. I mentioned force constant is represented by a dynes per centimeter and then one dyne approximately 1.02×10^{-3} grams (1.02×10^{-3}) gm. So this equation may be used to calculate approximate position of a band in the infrared spectrum by assuming that K for single double and triple bond is 5, 10 or 15 into 10^5 (10^5) dynes per centimeter (dynes/cm). That means for single bond you consider 5 into 10^5 (5×10^5), for double bond, consider 10 into 10^5 (10×10^5), and then triple bond, it is 15 into 10^5 (15×10^5), or if it is 500, given value should be 500 into 10^3 (500×10^3). We can simplify in this fashion. If we know this conversion and if you know how to convert stretching force constant to dynes per centimeter, we can use it, otherwise simply we can use the previous one. What I showed

is a much simplified one: $130.3 \sqrt{\frac{k}{\mu}}$. So, let us try this method here. For some simple molecules, for example, where C-C double bond is there, you can consider 10×10^5 (10 × 10⁵) dynes per centimeter (dynes/cm) or the value is also given here C double bond C stretching force constant is 960 that means 960×10^5 (960 × 10⁵) you can take then if you apply here of course this can be calculated here we get 6 here C double bond C this is what I have shown here in that table here and we can verify all the data to see authenticity of all the three equations and now by calculating by putting μ equals 6 and 10 for stretching force constant value comes around 1682 centimeter minus 1 (cm⁻¹), but if we use this one 9.60 it comes exactly 1648 very close to this experimental value. Of course, here, as I had mentioned, when the values are given in Newtons per meter so multiply this value into 10^3 (10³) and if it is 21 if you consider then it will be 21×10^5 (21 × 10⁵) and you can verify all these things, since we know the equation now. Three equations are there, you can just practice, since all the data is there. First you consider this as unknown entity. There is no point in considering this as unknown entity, because reduced mass can be easily calculated either you consider this as unknown entity or this one as unknown entity and you can verify from three equations to make yourself familiar in looking into the relationship between the stretching force constant and stretching frequency, that data obtained from IR spectroscopy. Let me take now another example: CH bond here, if you consider carbon atomic weight is 12 and hydrogen is 1, and if you put here what you get is 0.923 for C-H and of course, C-H this is the same value I have listed here, and then if you apply simply this equation, here what you get is calculated one, will be 3032 centimeter minus 1, but the experimental one is 3000 centimeter minus 1 (cm⁻¹). That means, this is the one calculated from this equation. How about considering C-D instead of C-H, then we have to take the exact value here. Then this also 10×10^5 (10 × 10⁵) here, single bond we are considering and then what we get here is 2228 centimeter minus 1. This is the calculated value we are getting and then here it is 2206 experimental value. Of course, if we take the exact value, it is very easy to achieve the experimental value here. Exact D atomic weight, if you consider then the reduced mass would vary little bit so that we can get the experimental value here. Now with this information, let us try to solve some problems.

Here is a question. Calculate the force constant of the P double bond O group in POCl_3 , oxyphosphorotrichloride, the strong infrared absorption band of the pure stretching vibration is observed at 1290 centimeter minus 1 (cm^{-1}). Now let us look into the simplest one. This one is $130.3 \sqrt{\frac{k}{\mu}}$. Consider P atomic weight 31 and for oxygen, it is 16. So, μ is P into O over P plus O atomic weights: This is 31 into 16 over 31 plus 16 ($\mu = \frac{31 \times 16}{31+16}$). This comes around 10.55. You can calculate. This is the value we get and here ν is given. We have to calculate the stretching force constant. 1290 equal to $130.3 \sqrt{k}$ is the unknown entity and here 10.55 and then to obtain this one, what we can do is, we can square entire stuff, so that we can remove the square root. This we can do by simply square, so we get this one. By simplifying this, we can get k or f. we can 1034.5 Newtons per meter (N/m). So, this is how we can get the value here and of course one should also know: one atomic mass unit equal to 1.67377×10^{-27} kgs (1.67377×10^{-27}). This we should use. If you want to use the next equation, We can do from this equation also.

For example, we can take this equation here. Let us consider this equation now μ equal to $\frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$, we know now, we have already calculated, and now ν square if we do, this one over $2\pi c$ whole square into k by μ so k becomes $1 \text{ by } 2\pi c$ whole square. Now if we add all the value here, In this one, what we should do is this, reduced mass, that should be converted into grams. So, if you multiply this one by one point six seven three seven seven into ten rise to minus twenty seven (1.67377×10^{-27}). This we should do it and after simplifying here what we get is, if you add all the values, one can get one zero four four point nine one Newtons per meter (N/m). This is how you can get it of course, here you can add everything which is known except for stretching force constant, that you can calculate using this method. Little difference comes, that is okay, that is allowed, and I would stay, stick to this method. This is rather easy. I use both either f or k. This is much simpler. I have to remember and also to perform the calculations.

Now another example is there. calculate the force constant of CO which shows a strong absorption at 2147 centimeter minus one (cm^{-1}) so here one can also do the calculation by

considering the previous one whatever i am considering here and this equation to just to make you familiar with all the methods so $\mu = \frac{m_1 m_2}{m_1 + m_2}$ and whatever the value comes that should be multiplied by this is six point eight five seven atomic mass unit it comes and this should be multiplied by one point six seven two three seven seven into ten rise twenty seven (1.67377×10^{27}) then it will be giving the value in kgs so here force constant we have to calculate as we did earlier μ if you put all the value here so you can find out the stretching force constant easily this comes around 1707.1 newtons per meter (N/m) you can put here of course 2.22×10^{22} by 7.3×10^{10} rise to 10 to this value this is 0.857 to 10 rise to minus 27 so this will give you value shown here so this is how you can use either this method or you can also go starting from a simple method such as $130.3 \sqrt{\mu}$ as I said k or f both will tell you force constant, stretching force constant; you should not worry much about this one as I said some books refers to k for force constant and some books refer to f for force constant. Now let's look into one more example here if the force constant of HCl is 521 newtons per meter (N/m), calculate this absorption frequency in centimeter minus one absorption frequency will be wave number so i mean atomic mass unit i have given here one point six seven three seven seven (1.67377) it can rise to minus 27 kg so this is needed if you want to use this equation here you have to convert that one if you want to use this one if you want to use other equation there is no need you can apply directly the values in newtons per meter so now let us consider here $130.3 \sqrt{521}$ reduced mass is going to be 0.9801 if you take here HCl H if I consider 1.008 into this one is 35.453 and then 1.008 you can get directly here value new one or you can make it square so that we can remove the square root or if we want to use the other equation this equation what we should do is we should multiply this value obtained in atomic mass unit into 1.67377 can rise to minus 27 and then we have to use this value in this one for new here once when we do that one we can get the approximately 2990 centimeter minus (cm^{-1}) one you can verify that one you can use both the methods and you should be able to get the correct value here. Now you can see in this table, I have given as I had mentioned, three methods are given. This is very convenient, this is also convenient provided you convert reduced mass after calculating or multiply this by 1.67377 into 10 rise to minus 27 (1.67377×10^{27}), your job is done, or you can use directly here only thing is, in this one, if you want to use $\bar{\nu} = \sqrt{\frac{f}{\mu}}$ into square root of f by μ

(f/μ), what you should do is, you should convert force constant from newtons per meter (N/m) to dynes per centimeter (dynes/cm) for that one you have to multiply by 10^3 rise to 3 (10^3), if it is two digit number or if it is four digit number, it should be multiplied by 10^5 rise to 5 (10^5). For example you take here you can multiply this one by 10^3 and you can do it we can do now for a simple one oh let us calculate nu 700 we have so from this one it is 130.3 square root of here f is given 700 by 0.94 so here if you multiply this one simply 27.288 it gives 355 5.7 centimeter minus one (cm^{-1}) so what we are getting is here 3600 what we are getting is 3555 centimeter minus one (cm^{-1}) and this looks fine.

Now let us look into other method. If you use this method, here what we should do is, we can simplify this the value. Simplified one is 3.5559 into 10^{22} (3.5559×10^{22}). After considering square root and then square root of 700 over 0.94 into 1.67377 into 10^{-27} looks like a little bit more complicated, but nevertheless, it is simple arithmetic. We are performing here and this would give you 125.1194 into 10^5 (10^5) and then this will be very close to 35 37 centimeter minus one (cm^{-1}). This is how we can do the calculation here

Let us look into C–C bond. Here C–C bond using this one 130.3 square root of C–C bond we are considering 425 by reduced mass is 6. This will give you 130.3 into 8.41625 and then multiplication will give you 1096.6 centimeter minus one. So, what we have is 1100. We have experimental, this is calculated and experimental is 1100. Like this, we can verify for all. So just to make yourself familiar by considering either force constant or stretching frequency as unknown entities and use all the three equations to understand these things so that you will not do any mistakes while calculating. What you should remember is, in this equation nothing you have to do. Simply you have to consider force constant in Newtons per meter, whereas here you have to consider again Newtons per meter, no problem, but after getting reduced mass, it should be multiplied by 1.67377 into 10^{-27} to convert that into kg in the other equation, where we are using 4.12 into square root of “f /mu” (f/μ). You multiply f by one into 10^3 or 10^5 ($f/1 \times 10^{-3}$ (or 10^{-5})) to make it dynes per centimeter. Let me come up with more examples in my next lecture until then have a good time thank you.