Chemistry II: Introduction to Molecular Spectroscopy

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Lecture - 17
Methodology of Solving Problems

Welcome back to the lectures on chemistry and in this series on the Introduction to Molecular Spectroscopy. I would like to put some problems sample problems, and also the method of solving them. Therefore, this is a video tutorial, and I hope it helps you to solve the regular tutorial problems of the course as well as towards the assessment in the final exam. These are elementary problems and what I have in this is about 10 sample exercises; and I shall indicate the method of solution not necessarily the final answer I think that you can calculate, but you have to relate the problem to the concept that was presented in the video. So, there is a question of thus there is a collection of 10 problems here.

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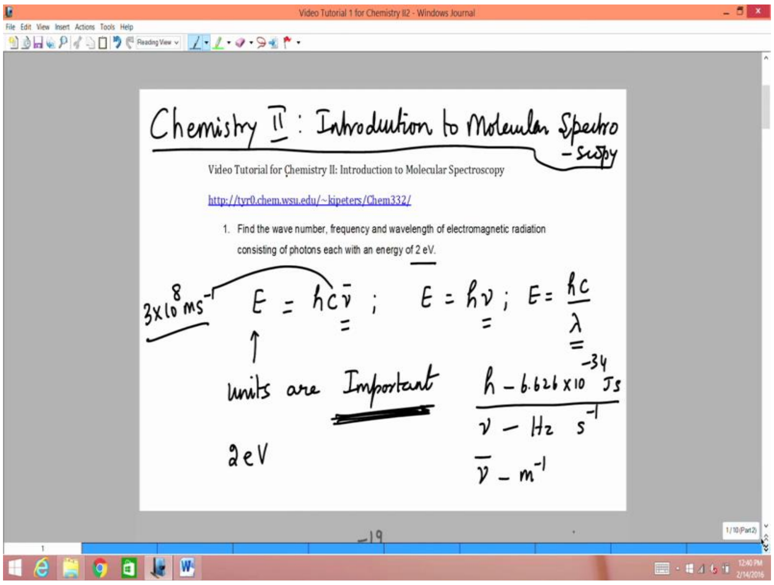

Chemistry II : Introduction to Molecular Spectro-scopy

Video Tutorial for Chemistry II: Introduction to Molecular Spectroscopy

http://tyr0.chem.wsu.edu/~kipeters/Chem332/

1. Find the wave number, frequency and wavelength of electromagnetic radiation consisting of photons each with an energy of 2 eV.

$3 \times 10^8 \, ms^{-1}$

$E = hc\bar{\nu}$; $E = h\nu$; $E = \frac{hc}{\lambda}$

units are Important

$h - 6.626 \times 10^{-34}$ Js

ν - Hz s^{-1}

$\bar{\nu}$ - m^{-1}

2eV

–19

And I also want to point out to the readers a very nice site that that I came across by professor Kipeterson of the State university of Washington, Washington State University, yes. And the site contains a large number of physical chemistry course problems which are useful to you. So, have a look at them. Now, let me read the first problem and then indicate to you what is the solution. The first problem asks you to find the wave number the frequency and wavelength of electromagnetic radiation consisting of photons each within energy of 2 electron moles. So, this is a very straightforward relation that you have to remember namely the energy of the photon is related to it is wave number by the Planck's constant and the speed of light times nu bar.

The second one is the energy related to the frequency in terms of the Planck's constant and the frequency. And the third is the energy related to the wavelength in an inverse fashion with the Planck's constant and the speed of the light and the wavelength dividing it. Therefore, you are asked to calculate nu bar, you are asked to calculate nu, and you are also asked to calculate lambda for a given energy. Units are important. Please underline this; the unit given to you is 2 electron volt for the energy. And remember Planck's constant h is in the unit of joule second 6.626 times 10 raise to minus 34 joule second, these are all SI units. And the frequency nu is in hertz or per second, and the wave number is in the unit of meter inverse, since they are all SI units.

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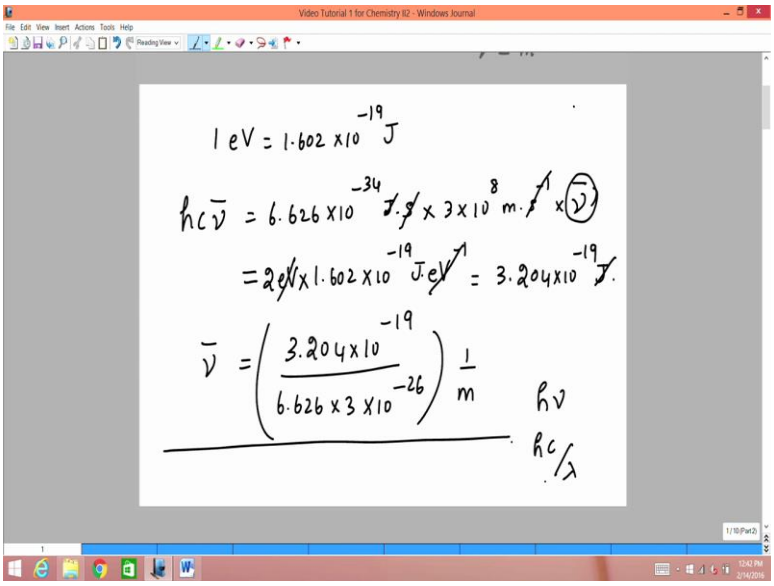

$$1\,eV = 1.602\times10^{-19}\,J$$

$$hc\bar{\nu} = 6.626\times10^{-34}\,J\cdot\cancel{s}\times3\times10^{8}\,m\cdot\cancel{s}^{-1}\times\boxed{\bar{\nu}}$$

$$= 2\,\cancel{eV}\times1.602\times10^{-19}\,J\cdot\cancel{eV}^{-1} = 3.204\times10^{-19}\,J.$$

$$\bar{\nu} = \left(\frac{3.204\times10^{-19}}{6.626\times3\times10^{-26}}\right)\frac{1}{m}$$

$h\nu$

hc/λ

The electron volt should; obviously be converted to joules you recall that 1 electron voltage 1.602 times 10 to the minus 19 joules. So, if you remember that then everything else is known to you h is given, c is given, therefore, nu bar can be calculated, h is given h is the Planck’s constant. So, it is easy to write, it is already written down here as 6.626 into 10 raise to minus 34. And the speed of light if you want to write that is for this calculation you can use the approximate value 3 into 10 to the 8 meters per second. So, everything is given, therefore, you only need to calculate the quantity nu.

So, the units are I will write one step for cancellation for h c nu bar as 6.626 times 10 to the minus 34 joule second, please write the units always in every such problem and c is given as 3 into 10 to the 8 meters per second, and you are asked to calculate nu bar. And the value given here is this is 2 e V or 1 e V, this is 2 e V, and therefore, the energy given is 2 times 1.602 into 10 to the minus 19 joules per e V. Please remember when you write the unit carefully these things cancel out in the correct manners. So, if you write this as to e V, and you write this as 1.602 times 10 to the minus 19 joules per e V, see the electron volt cancel. So, what you get is 3.204 times 10 to the power minus 19 joules and that is equal to 6.626 times 10 to the minus 34 joule second multiplied by 3 times 10 to the 8 meters per second, the second cancels off. And these are equated and therefore, you see that nu bar is going to be in terms of meter inverse namely, it is 3.204 into 10 raise to minus 19 divided by 6.626 into 3 into 10 to the minus 26. And the whole unit is 1 by meter. So, dimensions and units are extremely important. Therefore, in the similar manner you can calculate nu; you can calculate h c by lambda.

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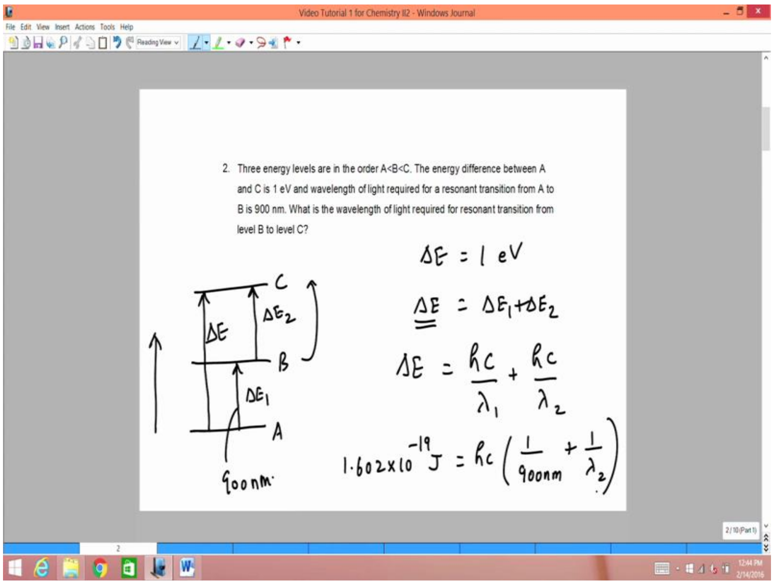

2. Three energy levels are in the order A<B<C. The energy difference between A and C is 1 eV and wavelength of light required for a resonant transition from A to B is 900 nm. What is the wavelength of light required for resonant transition from level B to level C?

$$\Delta E = 1\ eV$$

$$\underline{\underline{\Delta E}} = \Delta E_1 + \Delta E_2$$

$$\Delta E = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2}$$

$$1.602 \times 10^{-19} J = hc\left(\frac{1}{900nm} + \frac{1}{\lambda_2}\right)$$

Let us look at problem two. In the second problem, what is given are three energy levels in the order A less than B less than C meaning the energy state A is like this, B is like this, and C is like this and this is the increasing order of increasing energy. So, this is you call it as A, B, C. The energy difference between A and C is 1 electron volt; this delta E is given and that delta E is 1 electron volt. And the wavelength of right required light required for resonant transition from A to B is 900 nano meters, this lambda is given let me write it as delta E 1, and write this as delta E 2 then energy conservation tells you that the delta E should be equal to delta E 1 plus delta E 2. And you are given the wavelength for this transition as 900 nano meters. And you are asked to calculate what the wavelength of light required for resonant transition from B to C that is this transition.

Remember that delta E is inversely proportional to the wavelength. Therefore, this is delta E and this one is delta E 1 is given as 900 nano meters. Therefore, if you write h c by lambda 1 plus h c by lambda 2 and this is given as 1 electron volt. Therefore, what you have is 1.602 times 10 to the minus 19 joules on this side and that is equal to h c times 1 by 900 nano meters plus 1 by lambda 2.

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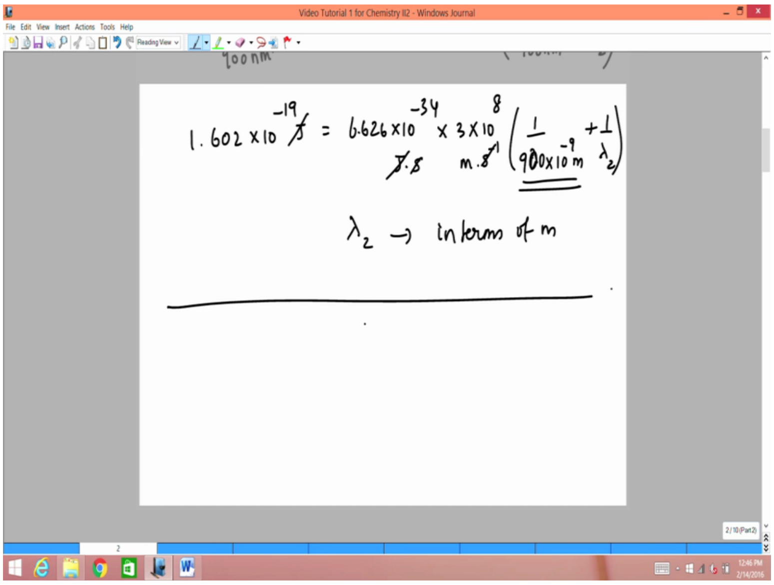

$$1.602\times10^{-19}\,\cancel{J} = \underset{\cancel{J}.\cancel{s}}{6.626\times10^{-34}} \times \underset{m.\cancel{s}^{-1}}{3\times10^{8}}\left(\frac{1}{\underline{\underline{900\times10^{-9}\,m}}}+\frac{1}{\lambda_2}\right)$$

$\lambda_2 \rightarrow$ in terms of m

Nano meters therefore, recall the units carefully you have 1.602 times 10 to the minus 19 joules and this is given as the sum of two energies 6.626 times 10 to the minus 34 times 3 times 10 to the 8. This is joules second and this is meters per second, and the joule and joule will go away, the second and second will go away, and what you have is 1 by 900 nano meters which is 900 into 10 to the minus 9 meter plus 1 by lambda 2. So, once you take care of the units properly, you see how everything cancels out correctly, and you can see that lambda 2 will be given in terms of meters. This is something easy to calculate, please do that completely, numerical exercise.

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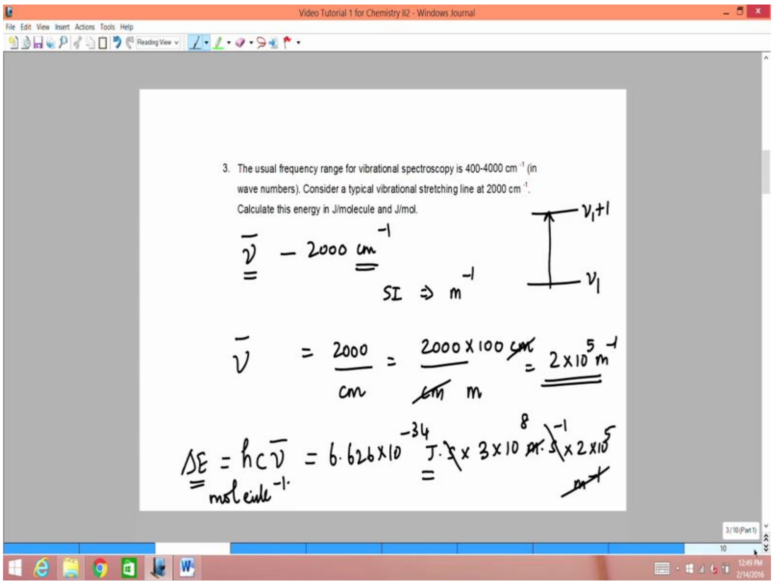

3. The usual frequency range for vibrational spectroscopy is 400-4000 cm^{-1} (in wave numbers). Consider a typical vibrational stretching line at 2000 cm^{-1}. Calculate this energy in J/molecule and J/mol.

$\bar{\nu} - 2000\ cm^{-1}$

$SI \Rightarrow m^{-1}$

$\nu_1 + 1$

ν_1

$$\bar{\nu} = \frac{2000}{cm} = \frac{2000 \times 100\ \cancel{cm}}{\cancel{cm}\ m} = 2 \times 10^{5}\ m^{-1}$$

$$\Delta E = hc\bar{\nu} = 6.626 \times 10^{-34}\ J.\cancel{s} \times 3 \times 10^{8}\ \cancel{m}.\cancel{s}^{-1} \times 2 \times 10^{5}\ \cancel{m^{-1}}$$

molecule^{-1}.

Third problem these are all very elementary problems. The purpose of discussing these problems in greater detail is to tell you the methodology of solving them and also algebraically how you have to pay attention to details even if they are trivial. Because at the end of it the (Refer Time: 09:59) is in the details, please understand that therefore, the solution of any problem you have to pay attention to all the details. So, here the third problem tells you the usual frequency range for vibrational spectroscopy is 400 to 4,000 centimeter inverse, this is in wave numbers, and you are given a typical vibrational stretching lying at 2,000 centimeter inverse.

And you are all asked to calculate the energy corresponding to this 2,000 centimeters inverse in 2 units; one as a joule per molecule and the other is as a joule per mole. A typical vibration refers to the change in energy in the single molecule 2,000 centimeter inverse means the energy required to raise the energy levels of a single molecule. Therefore, this nu bar, which corresponds to a transition between say some vibrational state due to the stretching line having a v 1 and v 1 plus 1, this corresponds to about 2,000 centimeters inverse. This is centimeter inverse; SI units are meter inverse.

Therefore, first of all you need to make sure that nu bar is expressed in the right unit, namely since it is 2,000 by centimeter it is essentially 2,000 into 100 centimeter per meter. So, that it is also centimeter here that cancels off. So, what you have is 2 into 10 raise to 5 meter inverse. So, this is the nu bar given to you. And you are asked to calculate the j joules per molecule and that is given as h c nu bar if everything else is expressed in the appropriate SI units. Therefore you do the same thing 6.626 times 10 to the minus 34 joule second times 3 into 10 to the 8 meters per second into 2 times 10 to the 5 per meter. So, you see that goes off then the meter, the second goes off that and what is left over is joules and this is per molecule.

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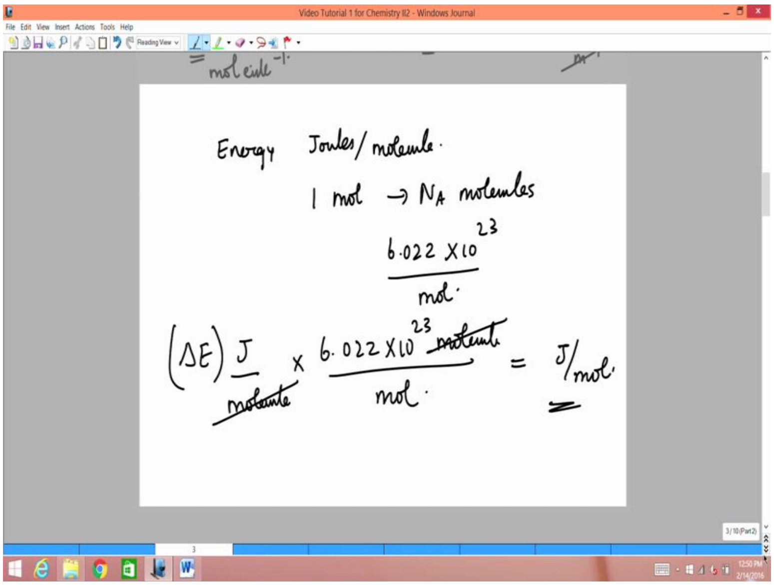

$= \text{molecule}^{-1}.$

Energy Joules/molecule.

$1 \text{ mol} \rightarrow N_A \text{ molecules}$

$$\frac{6.022 \times 10^{23}}{\text{mol}}.$$

$$(\Delta E)\frac{J}{\cancel{\text{molecule}}} \times \frac{6.022 \times 10^{23} \cancel{\text{molecule}}}{\text{mol}} = J/\text{mol}.$$

And what is the value for per mole. Whatever that you get energy in joules per molecule, since there are Avogadro number of molecules in 1 mole namely 6.022 times 10 to the 23 per mole, you can calculate the energy that you have done earlier. This number, you multiply this number by the Avogadro number then you get the energy per mol. Delta E joules per molecule into 6.022 times 10 to the 23 molecules per mol. So, you have that gives you joules per mol. So, dimensionally you see things look at these things carefully.

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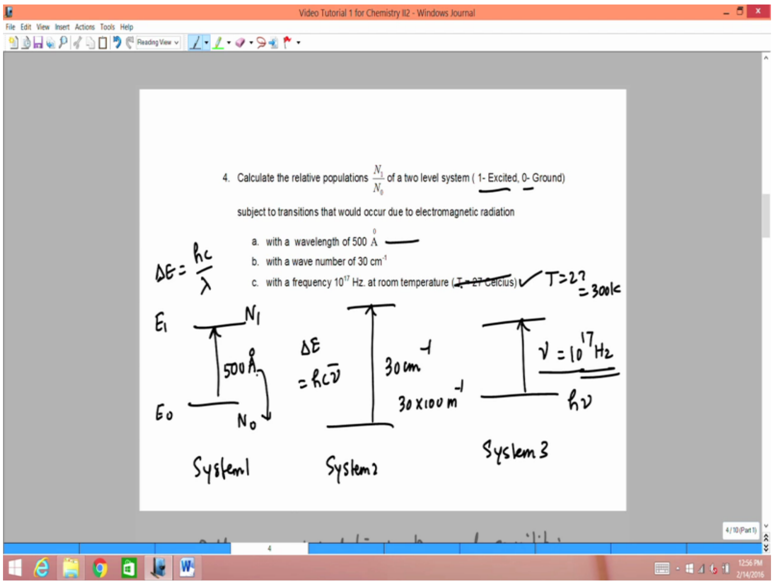

4. Calculate the relative populations $\frac{N_1}{N_0}$ of a two level system (1- Excited, 0- Ground) subject to transitions that would occur due to electromagnetic radiation

   a. with a wavelength of 500 $\mathring{A}$
   b. with a wave number of 30 cm^{-1}
   c. with a frequency 10^{17} Hz. at room temperature (~~T = 27 Celcius~~)

The next problem talks about the relative populations of molecules in a two level system. This is a model the level one is called the excited state, and the level zero is called the ground state, and N 1 corresponds to the number of molecules in the excited state, and the number N 0 corresponds to the number of molecules in the ground state. Therefore, you are asked to calculate the population ratio subject to transition that would occur due to electromagnetic radiation of three different types. Therefore, what you have in this problem is three different sets of energies, two level systems; this is one system E 0 E 1 with N 0 N 1.

This is system one corresponding to a transition of 500 angstroms, the transition energy requires a wavelength of 500 angstroms. This is another system, I am not worried about the scale, but I am simply writing this as system two corresponding to a transition of 30 centimeters inverse. This is system three except that here frequency is given as 10 to the 17 hertz. Again the temperature you will find out is an irrelevant data for this problem.

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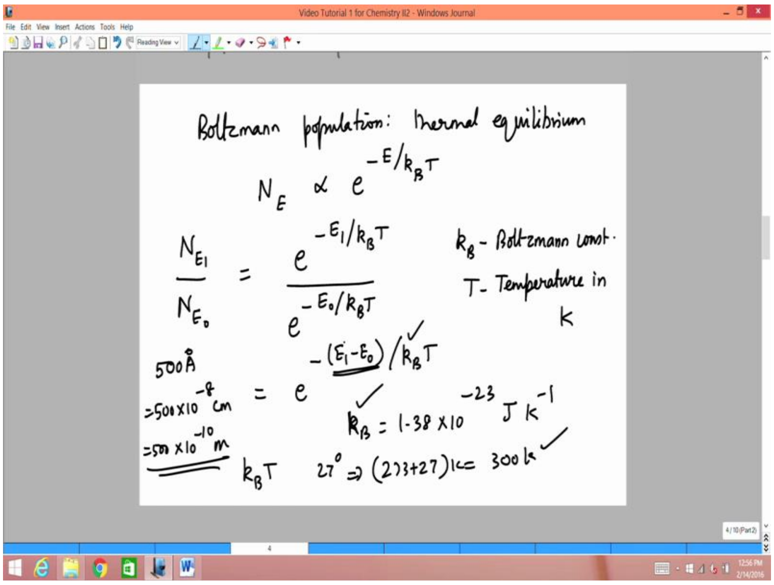

Boltzmann population: thermal equilibrium

$$N_E \propto e^{-E/k_B T}$$

$$\frac{N_{E_1}}{N_{E_0}} = \frac{e^{-E_1/k_B T}}{e^{-E_0/k_B T}}$$

k_B - Boltzmann const.

T - Temperature in K

$$= e^{-\underline{(E_1-E_0)}/k_B T} ✓$$

500 Å

$= 500 \times 10^{-8}$ cm

$= 500 \times 10^{-10}$ m

$k_B = 1.38 \times 10^{-23}$ J K^{-1} ✓

$k_B T$ $27^0 \Rightarrow (273+27)K = 300 K$ ✓

You are given three different units for the energies and you are asked to calculate N 1 by N 0. Please remember the Boltzmann population formula for thermal equilibrium, if the two energy levels are thermally at equilibrium with each other the molecules going up and down due to the absorption of energy and so on then immediately you should remember that the number of molecule which are in any particular energy state E is proportional to this ratio to this factor exponential minus E by k B T. If the energy level is non degenerate that is it is only one wave one function one state for 1 energy this is the formula.

And therefore, if you are looking at to the umber in the energy state E 1 versus the number in the energy state E 0, then you have to write to this as since proportionality constant is the same for both of them the ratio is exponential minus E 1 by k B T with exponential minus E 0 by k B T, where k B the Boltzmann constant so fundamental constant. And t is a temperature in Kelvin. Therefore, the answer is exponential E 1 minus E naught by k B T. If you go back to the problem you see one data point is missing here T is equal to 27 is important, we need that data T is equal to 27 or it is 300 Kelvin.

So, what you have is k B, is known k B is 1.38 times 10 to the minus 23 joules per

Kelvin therefore, k B T means that T should be in Kelvin. So, 27 degrees essentially means 273 plus 27 Kelvin which is 300 Kelvin. So, k B is known, T is known and delta E is given by the corresponding either the lambda or the nu bar or the nu. Please remember for this the delta E is h c by lambda; and for this the delta E is h c nu bar and for this the delta E is h nu. So, there are three different units used, and therefore, in each one of them you can calculate.

The only thing you have to remember is this angstrom; and angstrom refers to 10 raise to say if it is 500 angstrom, what it means is that 500 angstrom is 500 into 10 to the minus 8 centimeters or it is 500 into 10 to the minus 10 meters. You have to use SI units therefore, convert everything into meters seconds and joules. If energy is given in electron volts convert that into joules, if the energy is given in calories convert that into joules and then it is easy to use the SI unit and calculate the ratio exponential minus E 1 by E naught E 1 minus e naught is that delta E corresponding to this number. So, the lambda is 500 here multiplied by 10 to the minus 10 to give you the corresponding unit in meters. And this is 30 centimeter inverse therefore, you must multiply by 100 to give you meter inverse and this is in the right unit hertz, therefore you multiply by h. So, you can calculate delta E for this, delta E for this, and delta E for this you are three different models three different, what are called the pairs of energy levels therefore, you get three answers.

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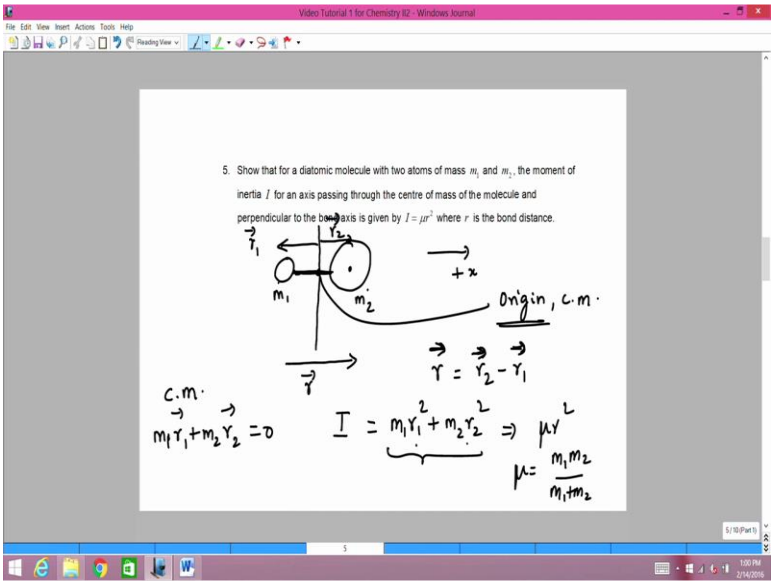

5. Show that for a diatomic molecule with two atoms of mass m_1 and m_2, the moment of inertia I for an axis passing through the centre of mass of the molecule and perpendicular to the bond axis is given by $I = \mu r^2$ where r is the bond distance.

$\vec{r} = \vec{r}_2 - \vec{r}_1$

c.m.

$m_1\vec{r}_1 + m_2\vec{r}_2 = 0$

$I = \underbrace{m_1 r_1^2 + m_2 r_2^2} \Rightarrow \mu r^2$

$\mu = \frac{m_1 m_2}{m_1 + m_2}$

The next problem this is something I had also mentioned in my lecture show that for a diatomic molecule with 2 atoms of mass m 1 and m 2. The moment of inertia I for an axis passing through the center mass of the molecule and perpendicular to the bond axis is given by the formula I is equal to mu r square. Now what is the picture, picture is you have a diatomic molecule with two different masses m 1 and m 2, the center of mass is closer to the heavier nucleus. And you are asked to calculate the moment of inertia about an axis, which is perpendicular to the bond axis. This is the bond axis. And this is the center of mass point the origin, for this system the center of mass.

And if you know that the radius vector of this atom from this origin is r 1 and the radius vector of the center of this atom from the origin is r 2 the inter atomic distance r. Let me write to the proper vector unit the inter atomic distance r is given that one direction is positive, suppose this is the positive x axis then r 2 is positive, but r is on the opposite sign, therefore r will be r 2 minus r 1 vectorially. And what is the moment of inertia, the moment of inertia is m 1 r 1 square plus m 2 r 2 square because r 1 and r 2 are the perpendicular distances of the two masses m 1 and m 2 from the axis about which we want to calculate the center of mass. So, m 1 r 1 square and m 2 r 2 square this is what is to be rewritten as mu r square where mu is the reduced mass m 1 m 2 by m 1 plus m 2.

And the distance vector r is related to the 2 vectors r 2 and r 1 by this choice. But also please remember the definition of the center of mass means the following that m 1 vector r 1 plus m 2 vector r 2 that should be 0 because the center of mass is also the origin. Therefore, if it is a pure vibration without the molecule moving anywhere then the pure vibration is essentially means of the center of the mass remains where it is that means this condition is satisfied for any vibrational amplitude r. For m 1 r 1 plus m 2 r 2 is 0 and vectorially and inter nuclear distance vector r is the difference r 2 minus r 1 because of the choice of the directions. With this, you have to do a simple substitution and get the answer. Let me write that now.

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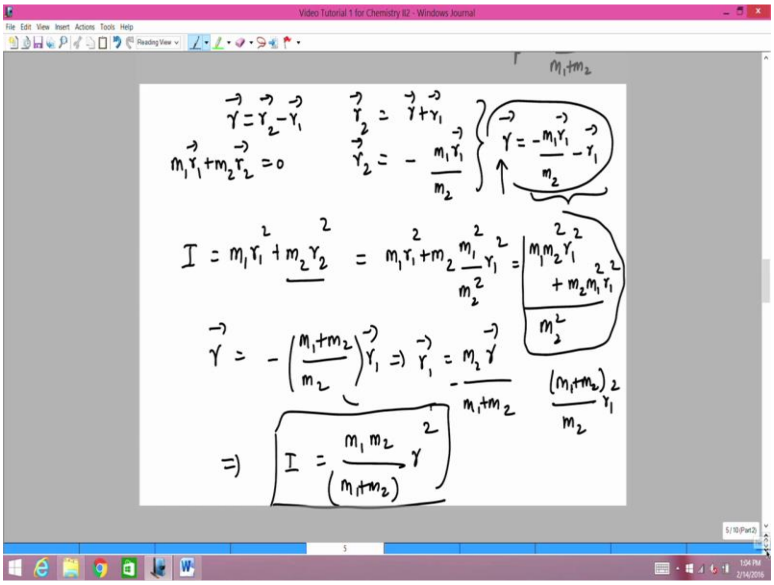

$$\vec{r} = \vec{r}_2 - \vec{r}_1 \qquad \vec{r}_2 = \vec{r} + \vec{r}_1$$

$$m_1\vec{r}_1 + m_2\vec{r}_2 = 0 \qquad \vec{r}_2 = -\frac{m_1\vec{r}_1}{m_2}$$

$$\boxed{\vec{r} = -\frac{m_1\vec{r}_1}{m_2} - \vec{r}_1}$$

$$I = m_1 r_1^2 + \underline{m_2 r_2^2} = m_1 r_1^2 + m_2 \frac{m_1^2}{m_2^2} r_1^2 = \boxed{\frac{m_1 m_2 r_1^2 + m_2 m_1^2 r_1^2}{m_2^2}}$$

$$\vec{r} = -\left(\frac{m_1+m_2}{m_2}\right)\vec{r}_1 \Rightarrow \vec{r}_1 = -\frac{m_2\vec{r}}{m_1+m_2} \qquad \frac{(m_1+m_2)2}{m_2} r_1$$

$$\Rightarrow \boxed{I = \frac{m_1 m_2}{(m_1+m_2)} r^2}$$

So, what you do is given the fact that r is r 2 minus r 1 think that is what I have written and so r 2 minus r 1 yes that is right r 2 is equal to r plus r 1. The condition that m 1 r 1 plus m 2 r 2 is equal to 0 gives you also r 2 is equal to minus m 1 r 1 by m 2. We substitute that you get the result namely r 2 is this value, r plus r 1 is that therefore from these two you can get the expression r is equal to minus m 1 r 1 by m 2 minus r 1, r 2 minus r 1 therefore, that is what you have. So, this is the definition of r using one vector r 1.

Now, I is m 1 r 1 square plus m 2 r 2 square. So, let us replace r 2 by whatever we have namely m 1 r 1 square plus m 2 times r 2 square which is m 1 square by m 2 square times r 1 square, these are scalars therefore, the minus sign goes away. And so what is left over is you have m 1. If you take the common factor, m 1 m 2 square, r 1 square plus m 2 m 1 square r 1 square divided by m 2 square. So, this you have to substitute the r 1 you have to substitute into this. If you do this substitution of r 1 as given here, using r, what is r 1, r is minus m 1 plus m 2 by m 2 times r 1 from this equation. Therefore, r 1 is m 2 r with the minus sign divided by m 1 plus m 2.

So, if you substitute r 1 square here, you will get immediately the expression that I is equal to m 1 m 2 by m 1 plus m 2 times r square. Please remember this is nothing other than m 1 plus m 2 by m 2 times r 1 square. So, substitute this and you get the moment of inertia I as this value. This is the standard expression. It is a very simple algebra, but that be vector notation has to be taken into account and you must know what is meant by the center of mass. This is used in rotational spectroscopy in diatomic molecular systems.

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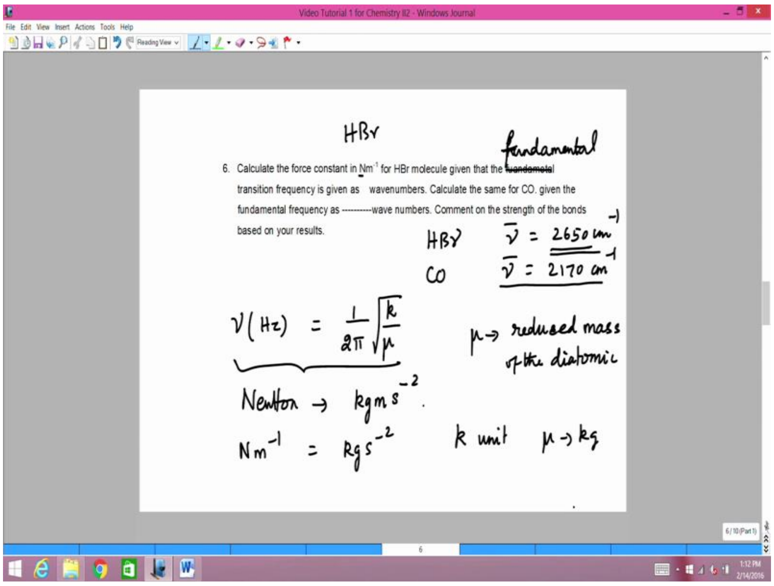

HBr

fundamental

6. Calculate the force constant in Nm^{-1} for HBr molecule given that the ~~fuandemetal~~ transition frequency is given as wavenumbers. Calculate the same for CO. given the fundamental frequency as ---------wave numbers. Comment on the strength of the bonds based on your results.

HBr $\bar{\nu} = 2650\ cm^{-1}$

CO $\bar{\nu} = 2170\ cm^{-1}$

$$\underbrace{\nu(Hz) = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}}$$

$\mu \rightarrow$ reduced mass of the diatomic

Newton $\rightarrow kg\,m\,s^{-2}$.

$Nm^{-1} = kg\,s^{-2}$

k unit $\mu \rightarrow kg$

Now, the next problem, in this problem we are asked to calculate the force constant in the unit of Newton per meter for the hydrogen bromide molecule. Given that the fundamental, the fundamental frequency is given as for HBR it is 2650 centimeter inverse, and also calculate the same for carbon monoxide that is the force constant given that the frequency is given as 2170 centimeter inverse. And you are also asked to calculate on the strengths of the bonds based on your result. First of all remember from the elementary vibrational spectroscopy that the fundamental frequency nu in hertz is given as 1 by 2 pi square root of k by mu, mu is the reduced mass of diatomic, k is the force constant. Remember the unit Newton that is basically kilogram meter per second square, force into distance is energy. So, given that Newton meter inverse is kilogram per second square that is the force constant k, the unit the reduced mass mu should be in kilograms. Therefore, nu will be square root of second to the minus 2 and so it is hertz. So, this is hertz you are given nu bar as 26 fifty centimeter inverse.

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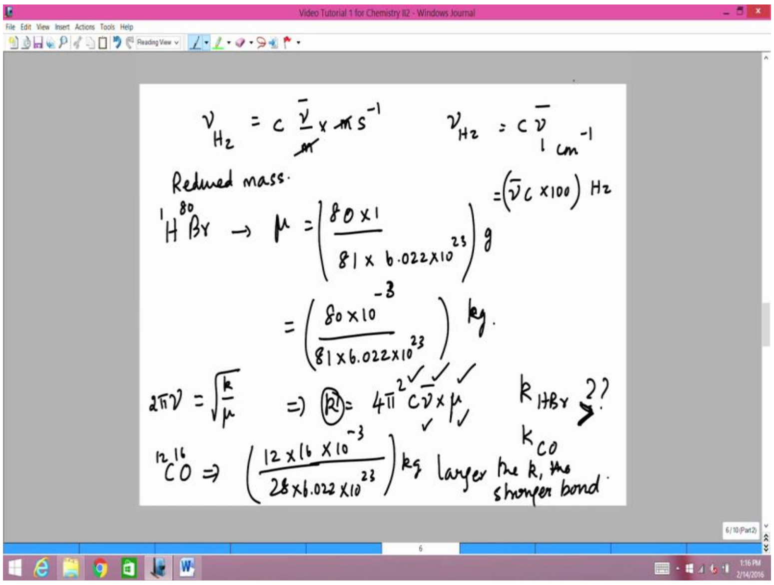

$\nu_{H_2} = c\,\frac{\bar{\nu}}{\cancel{m}} \times \cancel{m}\,s^{-1}$

$\nu_{Hz} = c\,\underset{1}{\bar{\nu}}\ cm^{-1}$

$= (\bar{\nu}\, c \times 100)\ Hz$

Reduced mass.

$^{1}H\,^{80}Br \rightarrow \mu = \left(\frac{80\times 1}{81\times 6.022\times 10^{23}}\right) g$

$= \left(\frac{80\times 10^{-3}}{81\times 6.022\times 10^{23}}\right) kg.$

$2\pi\nu = \sqrt{\frac{k}{\mu}} \Rightarrow \boxed{k} = 4\pi^{2} c\bar{\nu} \times \mu$

$k_{HBr}\ ?? > k_{CO}$

$^{12}C\,^{16}O \Rightarrow \left(\frac{12\times 16\times 10^{-3}}{28\times 6.022\times 10^{23}}\right) kg$ larger the k, the stronger bond.

Therefore, what is the relation between nu and nu bar please remember this is hertz. And I think you will remember this as per meter and it is meter per second which is the speed of light gives you per second. So, the relation is nu hertz is c nu bar, and nu bar is in centimeter inverse, since you are using SI units convert that as C nu bar into 100, you will get the hertz. So, these are the things you have to remember. What about the reduced mass, for HBR, if we use the atomic masses simply as 1 and 80 and that worried about the details you can actually put the exact number, but the process is 1 and 80. Then the reduced mass is 80 into one divided by 81 m 1 plus m 2 and this is has to be divided by 6.022 into 10 raise to 23 to get the mass of one molecule in grams. Therefore, you have to multiply this by 10 raise to minus 3 81 into 6.022 times 10 to the 23, so that would give you kilograms.

So, given then nu is equal to 2 pi nu is equal to square root of k by mu you get immediately k is equal to 4 pi square c nu bar, because that is nu times mu; c is known, nu bar is known in meter inverse, mu is known. Therefore, you calculate k, k you calculate for HBR k, you calculate for CO using the reduced mass for CO, this expression namely 12 carbon 16, 12 into 16 divided by 28 into 6.022 times 10 to the 23 and also multiply by 10 to the minus 3 to give you the kilograms. Therefore, for carbon monoxide, you know the mu, for carbon monoxide you are given the nu bar in centimeter inverse convert that into meter inverse put the c in meters per second, and then you see that you can calculate k, find out which is greater than which. The larger the force constant the stronger the bond larger the k the stronger the bond, therefore, you can find out which of the k the carbon monoxide or HBR is larger. And you will see this all the numerical results a numbers will be there in your websites along with the problems, but this is how I would like to pay attention to the details.

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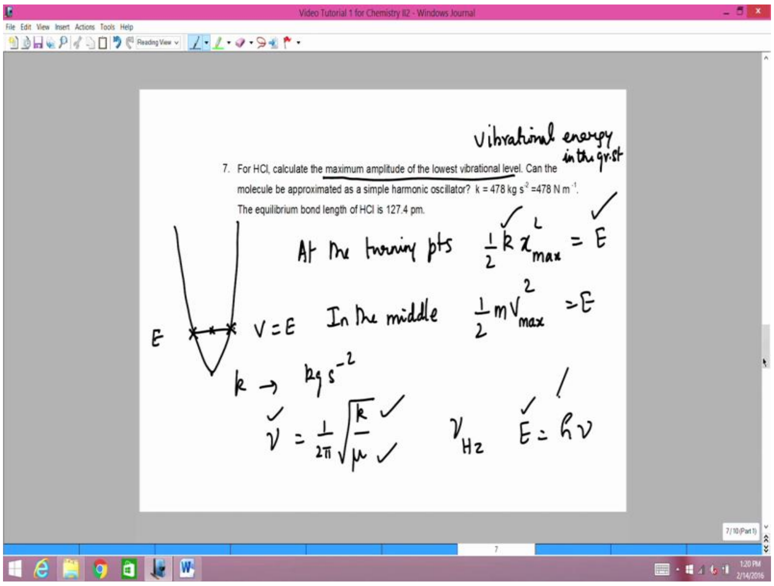

7. For HCl, calculate the maximum amplitude of the lowest vibrational level. Can the molecule be approximated as a simple harmonic oscillator? $k = 478\ kg\ s^{-2} = 478\ N\ m^{-1}$. The equilibrium bond length of HCl is 127.4 pm.

vibrational energy in the gr. st

At the turning pts $\frac{1}{2} k x_{max}^2 = E$

$V = E$ In the middle $\frac{1}{2} m v_{max}^2 = E$

$k \rightarrow kg\ s^{-2}$

$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ ν_{Hz} $E = h\nu$

Now, the next problem is something very similar. For hydrogen chlorine, calculate the maximum amplitude of the lowest vibrational level. Can the molecule be approximated as a simple harmonic oscillator and what are given you are given the force constant. And since the molecule is given as HCL you also know that the reduced mass can be calculated. What is meant by the maximum amplitude of the lowest vibrational level? What it means is that if the entire energy of the harmonic oscillator is vibrational potential energy, and it is equal to half k x maximum square. Please remember if you do a classical model, if this is the energy, these are called the turning points in the classical model corresponding to the maximum amplitude of vibration, where the potential energy is equal to the total energy. In the middle that is of the equilibrium position the molecule has no potential energy because we assume that the potential energy is zero at equilibrium distance therefore, the entire energy is kinetic energy. Therefore the molecule has the maximum vibrational velocity.

So, you have two conditions that at the turning points half k x maximum square, sorry this is x maximum square x maximum square that is equal to E and in the middle half m v max square is equal to E. So, if you are ask to calculate maximum vibrational amplitude where it means essentially the potential energy is all the total energy. And since you are given the value of k and you are given the value of E, you can calculate x max square, pay attention to the units. If in a similar problem, if somebody asks you what s the maximum vibrational velocity, what it means is that assuming that the molecule has no potential energy during that vibration meaning is right at the equilibrium during the vibration, what is the speed of the atom this is a classical model. So, either way you can calculate k is given as kilogram per second square.

Therefore, you can calculate E the equilibrium bond length is given. And in order to calculate E, you also need the vibrational energy in the ground state. Therefore, you need as an input vibrational energy in the ground state that can be calculated as remember the frequency in nu is 1 by 2 pi square root of k by mu since k is given, and mu can be calculated for HCL you know what the nu is. And once nu is known in hertz, the energy E is h nu therefore, the energy is known. And immediately you can write that this energy is whole half k x maximum square giving you x maximum is 2 e by k square root.

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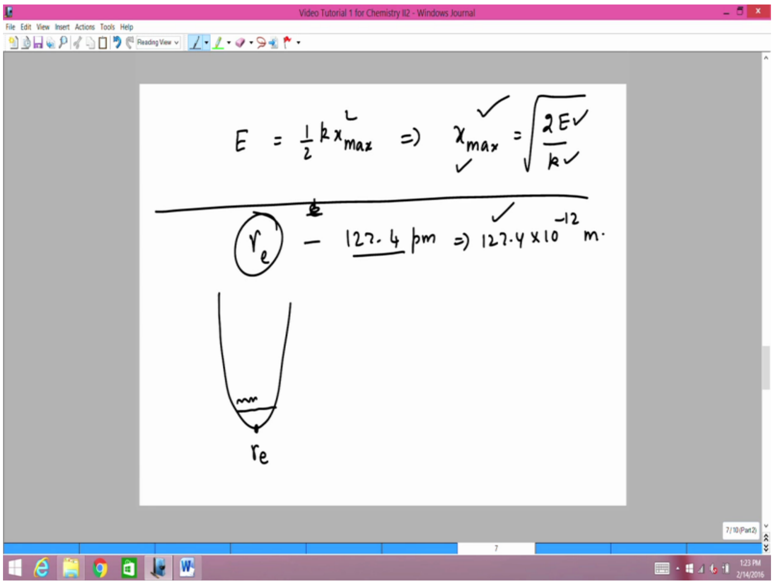

$$E = \frac{1}{2}kx_{max}^{2} \Rightarrow x_{max} = \sqrt{\frac{2E}{k}}$$

$$\boxed{r_e} - \underline{127.4}\ pm \Rightarrow 127.4 \times 10^{-12}\ m.$$

And if k is a known, E has been calculated therefore, x max can be calculated. Now, why are they given the data equilibrium bond distance? Equilibrium bond distance is 127.4 picometers. This is r equilibrium is 127.4 picometers meaning it is 127.4 into 10 raise to minus 12 meters. If you calculate x max and if the x max is very large compared to the equilibrium bond distance, then what it means is that the molecule at that lower energy level it is vibrational velocity is such that the harmonic model is meaningful. If however, the maximum bond length is very far away from the equilibrium, then you have to think about it, whether the vibrational the Young harmonocity, the harmonic model is appropriate to that of the equilibrium bond distance.

Therefore, at this energy if the maximum amplitude is very close to the bond distance then what it means is that the vibrational amplitude is not very different from is very small, and therefore, the equilibrium bond distance and the fully stretched vibrational molecule, the two bonds are very close to each other. For example, if this is that r e given by 127.4 and corresponding to this energy this number is a fraction of 127.4 if it is less than say 10 percent or 5 percent of 127.4 then it make sense that the vibration is harmonic because the amplitude of vibration is very small. If it is a very large number then the amplitude is very large; if the amplitude is very large then the harmonic model breaks down. Therefore, when you calculate x max, you will know how close it is to the equilibrium bond distance and that will give you the picture whether the molecular vibration that energy is nearly harmonic or not. So, you look at the numbers given in the website for solutions.

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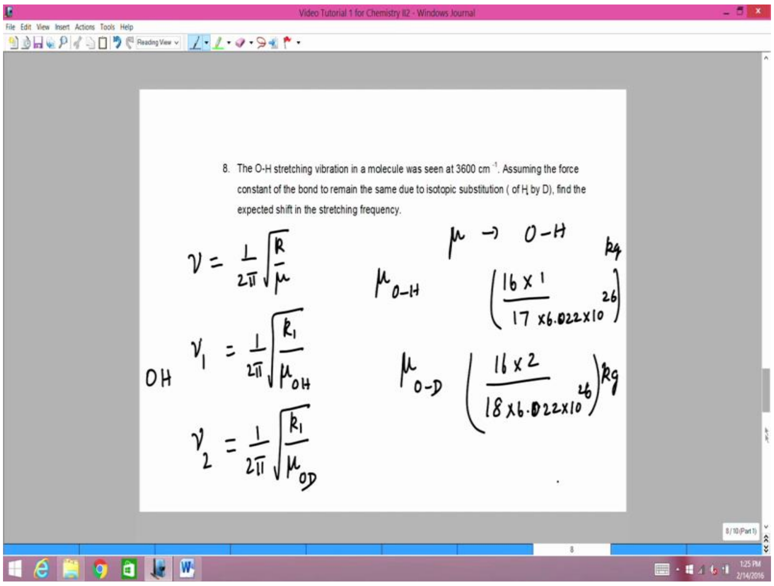

8. The O-H stretching vibration in a molecule was seen at 3600 cm $^{-1}$. Assuming the force constant of the bond to remain the same due to isotopic substitution (of H by D), find the expected shift in the stretching frequency.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\mu \rightarrow O-H$$

OH $$\nu_1 = \frac{1}{2\pi}\sqrt{\frac{k_1}{\mu_{OH}}}$$

$$\nu_2 = \frac{1}{2\pi}\sqrt{\frac{k_1}{\mu_{OD}}}$$

$$\mu_{O-H} \quad \left(\frac{16 \times 1}{17 \times 6.022 \times 10^{26}}\right) kg$$

$$\mu_{O-D} \quad \left(\frac{16 \times 2}{18 \times 6.022 \times 10^{26}}\right) kg$$

The next problem talks about the vibrational frequency dependence on the masses of the reduced masses of the atoms. And here the OH stretching vibration corresponding to the reduced mass species OH is about 3600 centimeters. So, if you write to the nu as 1 by 2 pi times k by mu this mu corresponds to mu of OH. Assuming that the force constant of the bond to remain the same due to isotopic substitution of h by b. So, let us call this as nu one corresponding to OH. We are asked to find out the expected shift in the stretching frequency.

So, if this is nu 1, it is 1 by 2 pi k 1 by mu OH. You are told that the force constant is the same, therefore, if there is any difference in the vibrational stretching frequency, it is due to the fact that it is k 1 by mu OD. The reduced mass of OD and OH are different. Please remember OH is 16 into 1 by 17 times 6.022 times 10 to the 26, if you want to write this in kilograms whereas, the mu of OD, if you remember is 16 into 2 by 18 16 plus 2 times 6.022 into 10 to the 26 kilogram. Therefore, the mu of OD and the mu of OH are quite different and since it is isotopic substitution if the force constant remains the same, the bond strength is very much the same then what is the shift in nu one due to the substitution.

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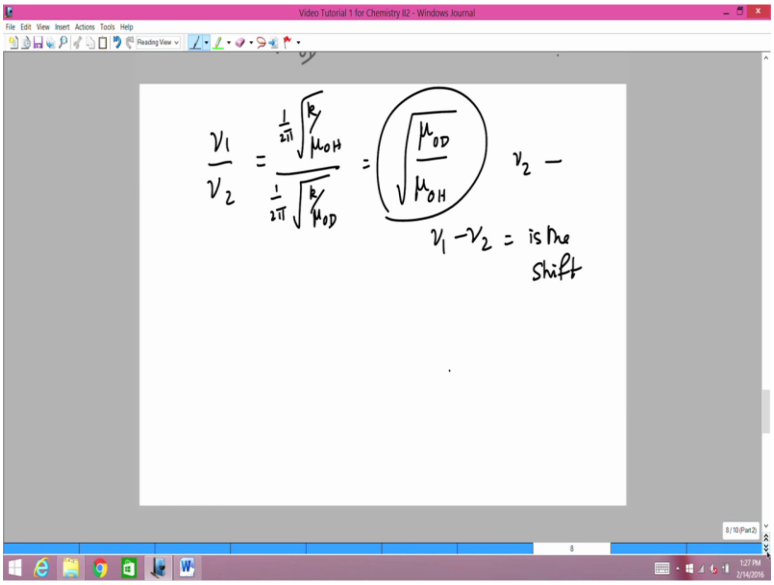

$$\frac{\nu_1}{\nu_2} = \frac{\frac{1}{2\pi}\sqrt{k/\mu_{OH}}}{\frac{1}{2\pi}\sqrt{k/\mu_{OD}}} = \boxed{\sqrt{\frac{\mu_{OD}}{\mu_{OH}}}} \quad \nu_2 -$$

$\nu_1 - \nu_2$ = is the shift

Therefore, you are only calculating the ratio nu 1 by nu 2 as 1 by 2 pi square root of k by mu OH divided by 1 by 2 pi square root of k by mu OD. And obviously, after canceling what you see is mu OD by mu OH. So, you can see the ratio nu 1 and nu 2 and therefore, if nu two is substantially different from nu 1, you can see that this number OD is bigger than the number mu OH. And therefore, the nu 1 for OH is more than that for nu 2 the vibrational frequency is reduced when you substitute with the heavier mass and because it is inversely proportional to reduced mass. And you can see immediately that nu two will be different, what is the difference between nu 1 and nu 2 that is the shift in the vibrational frequency. So, substitute the numbers here and you will immediately get the answer.

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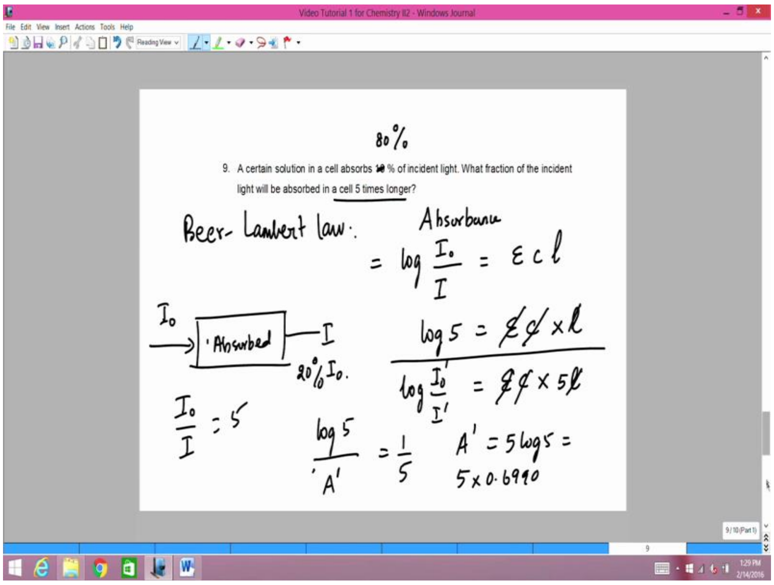

80%

9. A certain solution in a cell absorbs ~~10~~ % of incident light. What fraction of the incident light will be absorbed in a cell 5 times longer?

Beer- Lambert law:

Absorbance $= \log \frac{I_0}{I} = \varepsilon c l$

$I_0 \rightarrow$ Absorbed $- I$

$20\% I_0$.

$\frac{I_0}{I} = 5$

$$\frac{\log 5 = \cancel{\varepsilon}\cancel{c} \times l}{\log \frac{I_0'}{I'} = \cancel{\varepsilon}\cancel{c} \times 5\cancel{l}}$$

$\frac{\log 5}{A'} = \frac{1}{5}$

$A' = 5 \log 5 =$

5×0.6990

The next problem is on the Beer-Lambert law. A certain solution in cell absorbs 10 percent of incident light. What fraction of the incident light will be absorbed in a cell five times longer? I think I changed that number from 10 to 80 percent just to get some logarithmic ratios reasonable 80 percent of incident light. So, recall the Beer-Lambert law that the absorbent which is the logarithm of incident intensity of light to the intensity of light that is emitted that is the molar extension coefficient epsilon times concentration of the substance times the length of the cell. Now, when you say a cell absorbs 80 percent of incident light what it means is that obviously, when I naught and I are looked at I is 20 percent of I naught, because the rest is absorbed. So, when 80 percent is absorbed what you means is 20 percent is transit transmitted, therefore, I naught by I is 5.

So, you know log 5 is sum epsilon for that substance times it is concentration times the length of the cell. Now, you are asked to calculate what is the corresponding log I naught prime by I prime, sorry if the concentration of the cell remains the same concentration of the substance remains the same then the length becomes the five times the length of the cell a cell five times longer. So, you can calculate this number by taking the ratio, because this goes away this goes away this in the ratio when you divide, the length also goes away. So, what you have is log 5 by A prime due to the five times longer length is 1 by 5. Therefore, you can calculate a prime as 5 times log 5 log 5 is 0.6990. So, you have

5 times 0.6990 that is A prime.

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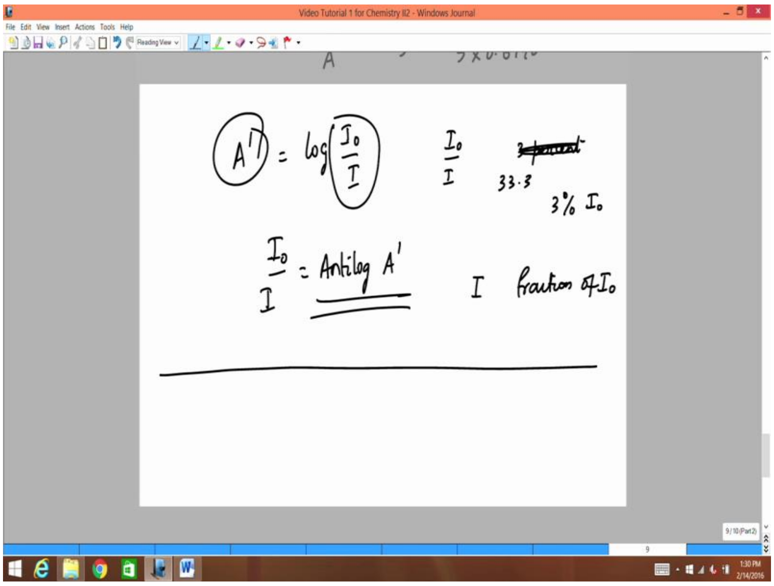

$\boxed{A'} = \log\left(\frac{I_0}{I}\right)$

$\frac{I_0}{I}$ ~~3 percent~~ 33.3

3% I_0

$\frac{I_0}{I} = \underline{\underline{\text{Antilog } A'}}$

I fraction of I_0

But what is A prime, A prime is log I naught by I. Therefore, from this taking the antilogarithm of this value you can calculate I naught and the ratio I naught by I. So, if the ratio for example is 3 percent if what it means is that the ratio is not 3 percent if the ratio is 33.3, what it means is that 3 percent of I naught gets transmitted the remaining 97 percent gets absorbed. Therefore, based on the antilogarithm you can calculate I naught by I as anti log A prime. And from this, you can get the value of I as the fraction some of I naught. So, this number will also be there in the text.

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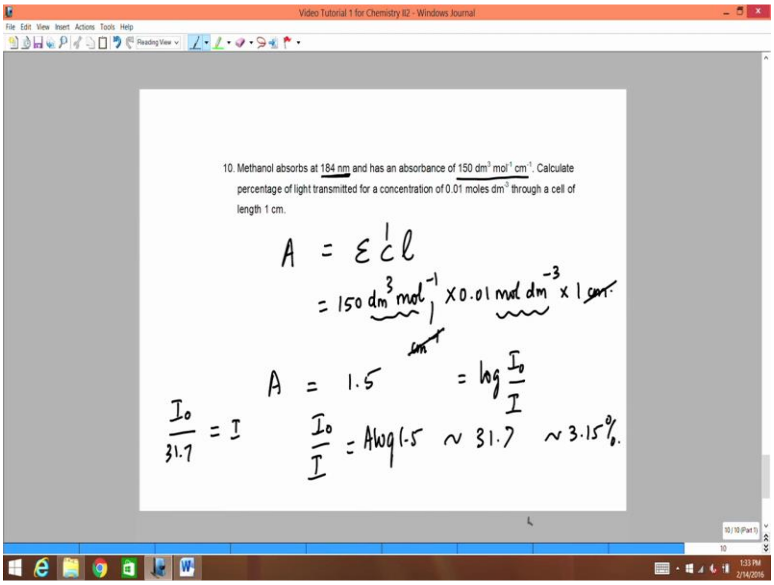

10. Methanol absorbs at 184 nm and has an absorbance of 150 dm^3 mol^{-1} cm^{-1}. Calculate percentage of light transmitted for a concentration of 0.01 moles dm^{-3} through a cell of length 1 cm.

$$A = \varepsilon c l$$

$$= 150\,\mathrm{dm^3\,mol^{-1}}\,\cancel{\mathrm{cm}^{-1}} \times 0.01\,\mathrm{mol\,dm^{-3}} \times 1\,\cancel{\mathrm{cm}}$$

$$A = 1.5 \qquad = \log \frac{I_0}{I}$$

$$\frac{I_0}{31.7} = I \qquad \frac{I_0}{I} = \mathrm{Alog}\,1.5 \sim 31.7 \quad \sim 3.15\%.$$

The last problem is again on Beer-Lamberts law, and it talks about another compound methanol absorbing at a particular frequency particular light wavelength, and it has some absorbance of 150 dm cube per mol per centimeter. So, absorbance is a given by epsilon into concentration length l epsilon is given as 150 dm cube per mol. And the concentration of the cell is given as 0.01 mol per dm cube; and the length of the cell this is c, and the length of the cell is 1 centimeter, there is also here per centimeter. So, dimensionally absorbance is has no dimensions that cancels are and the dm cube mol inverse is the inverse of the mol dm cube. So, what you have is 1.5, absorbance is 1.5.

And what is the percentage of light transmitted this is equal to log I naught by I. And in this case, if I look at the numbers I think it is about thirty one point that is I naught by I is A log of 1.5 it is about 31.7. So, what it means is that I is 31.7 times less than I naught. So, the percentage of light that comes out is roughly 3.15 percent because that is what it is I naught by 31.7 will be I and that is 3.15 percent of the original I naught. So, these are simple ways of manipulating elementary exercise of course, you have to learn more and more about the computations of small parameter as well as the numerical parameters that you need to calculate in solving these problems.

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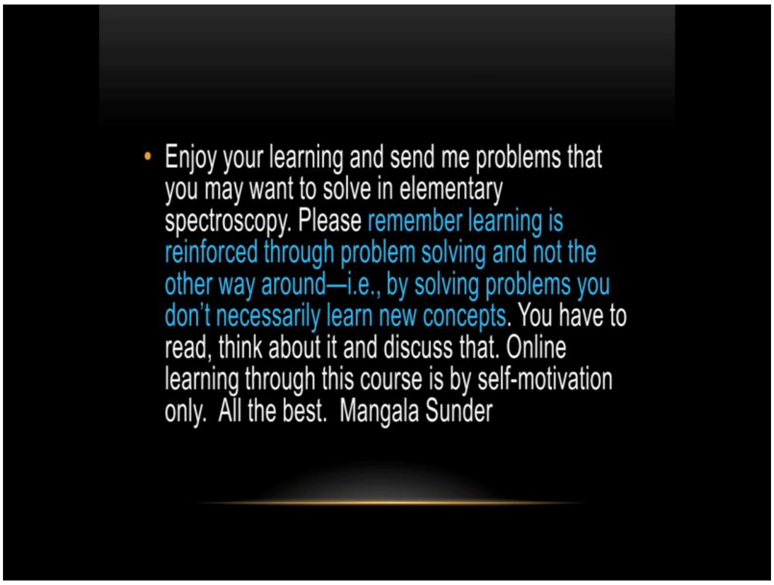

- Enjoy your learning and send me problems that you may want to solve in elementary spectroscopy. Please remember learning is reinforced through problem solving and not the other way around—i.e., by solving problems you don't necessarily learn new concepts. You have to read, think about it and discuss that. Online learning through this course is by self-motivation only. All the best. Mangala Sunder

And let me share with you the last slide of the PPT, which contains these problems in text form for you. Let me go to the presentation last slide is quite important, most important. Whatever you do you have to enjoy your learning, and if there are problems of similar nature that you want to solve in this course by looking at text books and other sites, please do send and share them with the other students in the website. But please remember even though I have given you a tutorial, please remember learning is only reinforced through these problem solving methods it is not the other way around, you do not learn by solving problems.

Your learning is through understanding concept thinking about it and discussing that, problems ensure that the way you have understood that is reinforced by solving them right. Therefore, please remember learning is only reinforced through problem solving, it is important that problem solving is necessary, it is not a sufficient exercise to understand a subject. Therefore, please read more please listen to the lecture, please find your own problems and online learning through this course or by any other course on your own is actually by self-motivation. And while I continue to solve similar problems I wish you all the best.

Thank you.