Spectroscopic Techniques for Pharmaceutical and Biopharmaceutical Industries
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Lecture No. 12
Problems on Rotational, Vibrational & Raman Spectroscopy

Hello students, welcome to lecture 12 of this course, the last 5 lectures I have discussed about rotational spectroscopy, vibrational spectroscopy, rotational-vibrational spectroscopy and Raman spectroscopy. We have looked at both theory and application of these spectroscopy techniques. In this lecture, I will discuss about problems related to this spectroscopy.

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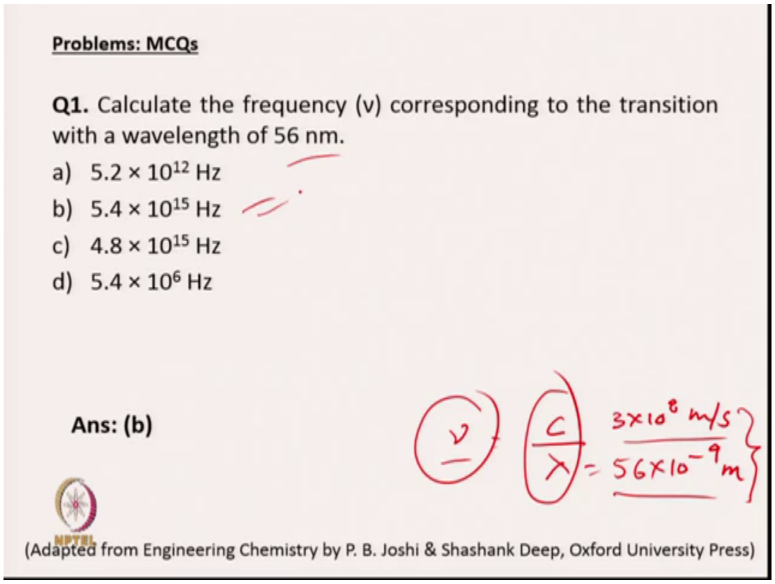

Problems: MCQs

Q1. Calculate the frequency (ν) corresponding to the transition with a wavelength of 56 nm.

a) 5.2 × 10^{12} Hz

b) 5.4 × 10^{15} Hz

c) 4.8 × 10^{15} Hz

d) 5.4 × 10^{6} Hz

Ans: (b)

$$\nu = \frac{c}{\lambda} = \frac{3\times10^{8}\ m/s}{56\times10^{-9}\ m}$$

(Adapted from Engineering Chemistry by P. B. Joshi & Shashank Deep, Oxford University Press)

So, I will start with multiple choice question, first question is quite easy that tells you what frequency if wavelength is given. So, question is calculate the frequency corresponding to the transition with wave length of your 56 nanometer. So, we know that frequency related to c by lambda where c is your velocity of light and lambda is your wavelength lambda is given it is 56 nanometer, it means that 56 into 10 per to power minus 9 meter. If you, we calculate this will get the frequency in per second which is basically hertz. So, it is quite easy question and if you do calculation and what will you get is 5.4 into 10 to power 15 hertz. So, this is the frequency of light of wavelength 56 nanometer.

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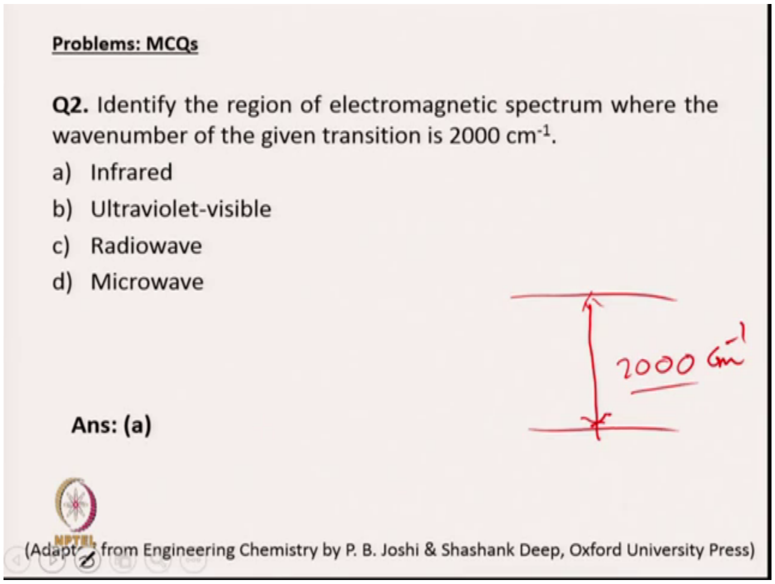

Problems: MCQs

Q2. Identify the region of electromagnetic spectrum where the wavenumber of the given transition is 2000 cm^{-1}.

a) Infrared

b) Ultraviolet-visible

c) Radiowave

d) Microwave

Ans: (a)

2000 cm^{-1}

(Adapted from Engineering Chemistry by P. B. Joshi & Shashank Deep, Oxford University Press)

Now, let us go to second question in this you have to identify the region of electromagnetic spectrum where the wave number of given transition is 2000 centimeter inverse. So, these are the 2 energy states and you have to tell that, if they have number of given transition is 2000 centimeter inverse, then what is the region of electromagnetic spectrum? And this is, this you have to know because the wavelength corresponding to 2000 centimeter inverse falls in IR region and so answer is infrared region.

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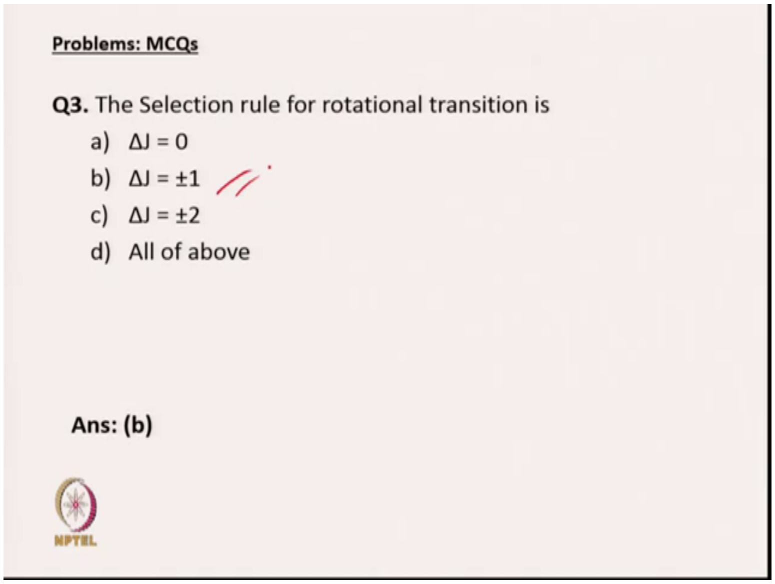

Problems: MCQs

Q3. The Selection rule for rotational transition is

a) $\Delta J = 0$

b) $\Delta J = \pm 1$

c) $\Delta J = \pm 2$

d) All of above

Ans: (b)

The next question is what is the selection rule for rotational transition and what is the selection rule for rotational transition? There are 4 option delta J is equals zero, delta j is equal to plus minus 1, delta J is equal to plus minus 2 and the all of the above we have already discussed this in our previous lecture. So, we know that selection rule for rotational transition is delta J is equal to plus minus 1. So, answer will be b.

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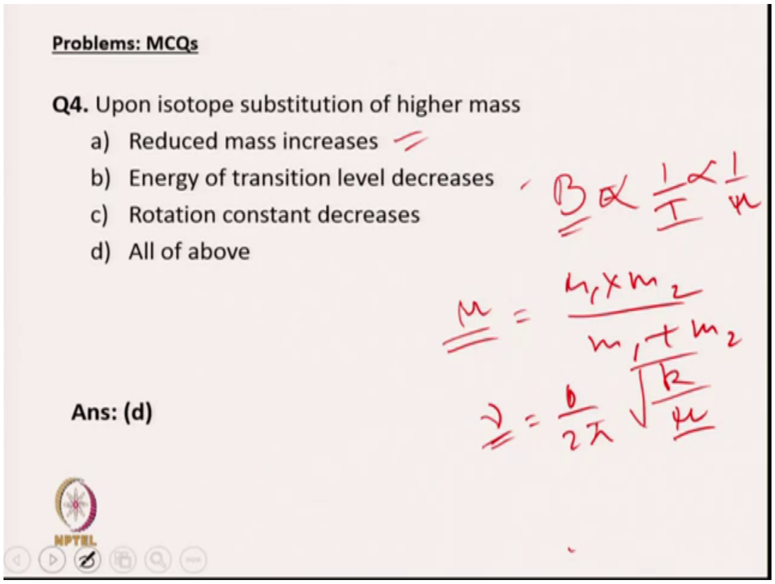

Problems: MCQs

Q4. Upon isotope substitution of higher mass

a) Reduced mass increases

b) Energy of transition level decreases

c) Rotation constant decreases

d) All of above

Ans: (d)

$$\underline{\underline{B}} \propto \frac{1}{I} \propto \frac{1}{\mu}$$

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

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

Next question is upon isotope substitution of higher mass what happens? Reduced mass increases, energy of transition level decreases, rotational constant decreases, all of the above. So, we need to know how to write to reduced mass and we know that it is mass is m1 into m2 divided by m1 plus m2, m1 plus m2 and so, if we substitute an element with its isotope with higher mass what we are going to get is your increase in reduced mass and then we know that frequency of your transition is equal to 1 by 2 pi root k by mu.

So, here your reduced mass will increase and if reduce mass increases, your frequency will decrease. So, this is also right and then about rotational constant, so, b is equal to, so, we need to know what is B and B is inversely proportional to your 1 by I and since I relates to mu, you can also write 1 by mu and so your B will decrease with increase in mu which in reduced mass. So, basically all of the above that d option is correct.

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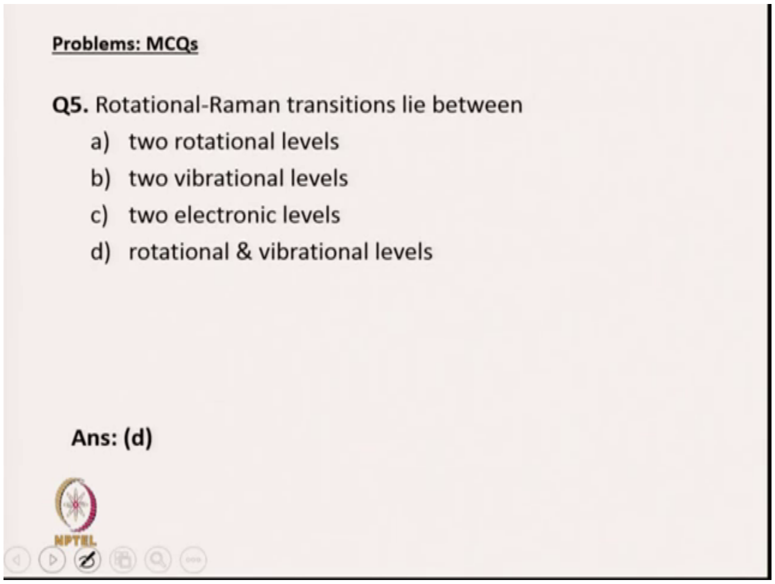

Problems: MCQs

Q5. Rotational-Raman transitions lie between

a) two rotational levels
b) two vibrational levels
c) two electronic levels
d) rotational & vibrational levels

Ans: (d)

Now, next question is the rotational Raman transitions lie between, 2 rotational levels, 2 vibrational levels, 2 electronic levels and rotational and vibrational levels. So, if you remember rotational Raman transition, you will be able to answer this question very easily and the answer is your d.

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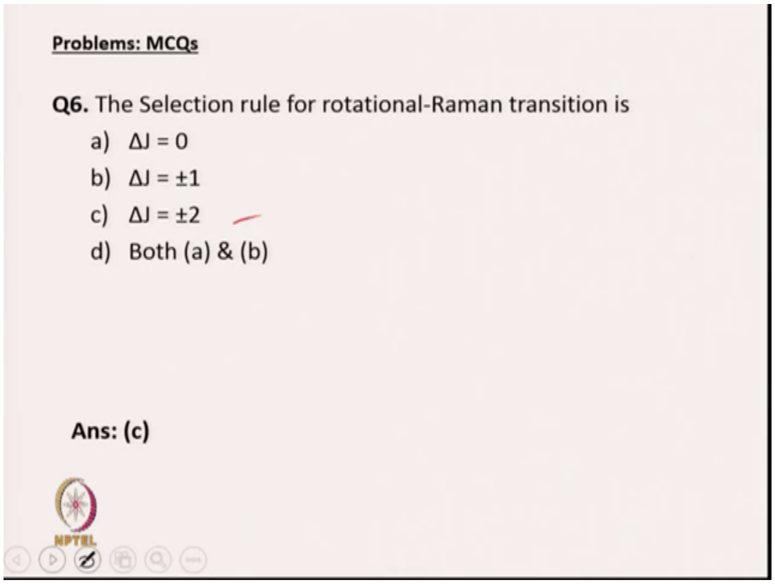

Problems: MCQs

Q6. The Selection rule for rotational-Raman transition is

a) $\Delta J = 0$
b) $\Delta J = \pm 1$
c) $\Delta J = \pm 2$
d) Both (a) & (b)

Ans: (c)

Now, next question is what is the selection rule for rotational Raman transition. So, the options given are delta J is equal to zero, delta J is equal to plus minus 1, delta J is equal to plus minus 2 and these both A and B to answer is your delta J is equal to plus minus 2. I have discussed this in detail in the rotational Raman transition and it was quite clear that why delta J should be equal to plus minus 2. So, answer is c.

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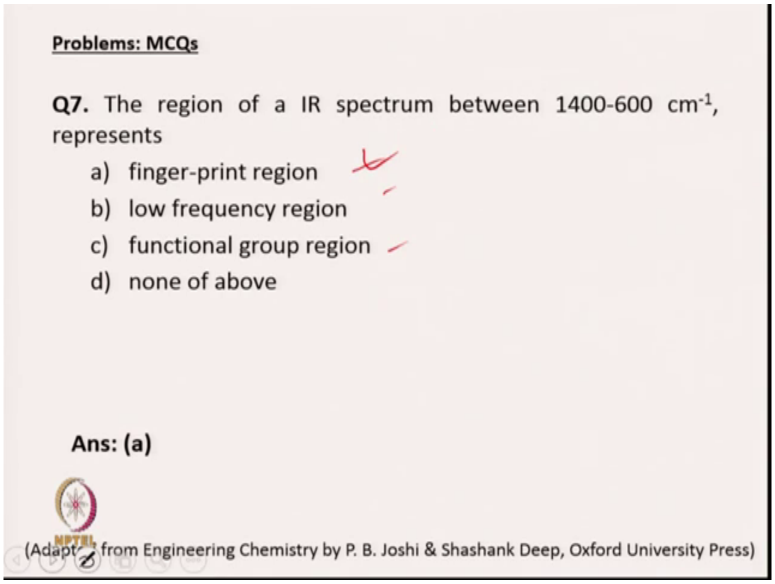

Problems: MCQs

Q7. The region of a IR spectrum between 1400-600 cm^{-1}, represents

a) finger-print region ✓
b) low frequency region
c) functional group region
d) none of above

Ans: (a)

(Adapted from Engineering Chemistry by P. B. Joshi & Shashank Deep, Oxford University Press)

Now, you go to a specifics of IR spectrum and next question based on that question is the region of IR spectrum between 1400 to 600 centimeter inverse represents. So, these are the regions fingerprint region, low frequency region, functional group region and none of the above and the answer is fingerprint region. And this is very important region if you want to get a structural feature of the molecule using IR spectroscopy.

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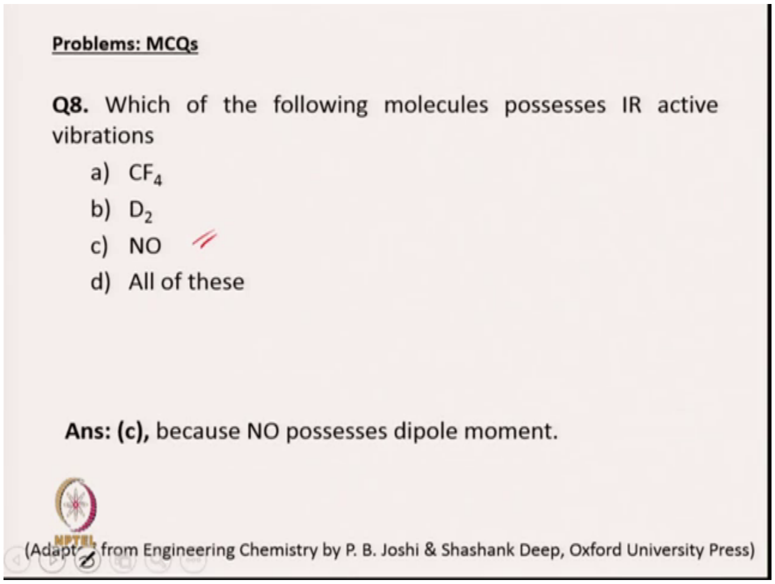

Problems: MCQs

Q8. Which of the following molecules possesses IR active vibrations

a) CF_4
b) D_2
c) NO
d) All of these

Ans: (c), because NO possesses dipole moment.

(Adapted from Engineering Chemistry by P. B. Joshi & Shashank Deep, Oxford University Press)

Which of the following molecule possesses IR active vibration? So, next question is based on the selection rule, you must know what is the selection rule for vibrational spectroscopy and rotational spectroscopy and the things we know is that dipole moment of the molecule must change during the vibration. So, in this the one which possesses IR active vibration is NO, NO, because its dipole changes during the vibration.

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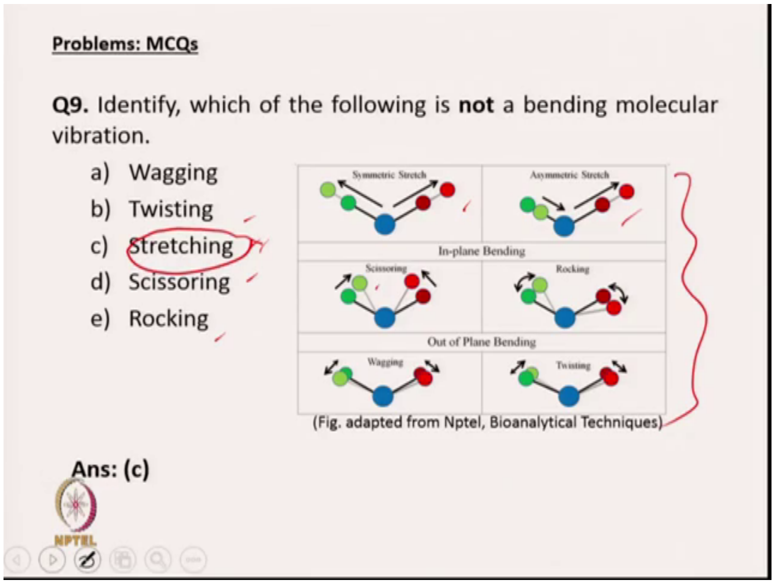

Problems: MCQs

Q9. Identify, which of the following is **not** a bending molecular vibration.

a) Wagging
b) Twisting
c) Stretching
d) Scissoring
e) Rocking

(Fig. adapted from Nptel, Bioanalytical Techniques)

Ans: (c)

Now, next question is, identify which of the following is not bending molecular vibration. So, there are 5 different kind of vibration is given one is wagging, then twisting, stretching, scissoring, rocking, and we know that stretching is not a bending vibration a stretching is not a bending vibration. So, answer is c, you have a stretching, symmetric stretching vibration.

This is your asymmetric stretching vibration in plane bending. So, in plain bending can be up to type scissoring and rocking. So, scissoring both are moving in towards each other. Whereas, in rocking, there is like rocking between 2 different position. Out of plain bending and out of plain bending will be again of 2 types and your wagging and twisting, the wagging and twisting. So, you must remember these different types of vibrational modes in this wagging, twisting visiting and rocking are type of bending molecular vibration while stretching not so, answer is c.

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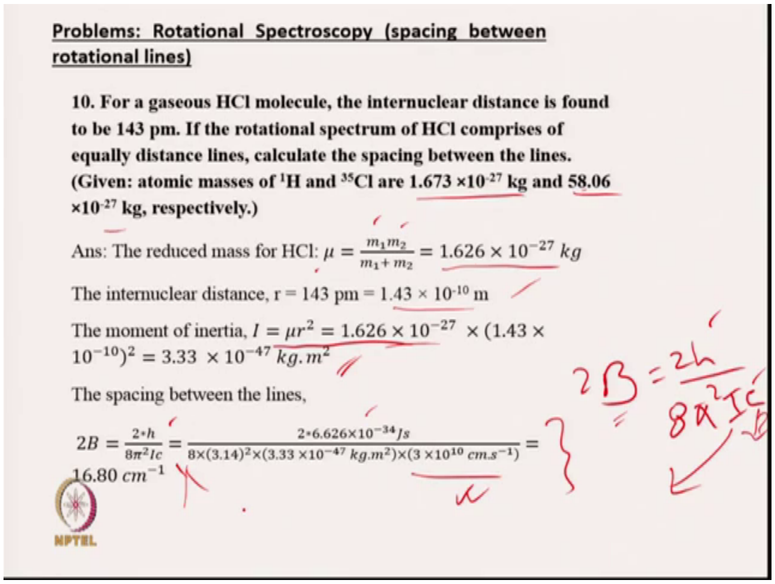

Problems: Rotational Spectroscopy (spacing between rotational lines)

10. For a gaseous HCl molecule, the internuclear distance is found to be 143 pm. If the rotational spectrum of HCl comprises of equally distance lines, calculate the spacing between the lines. (Given: atomic masses of ^1H and ^{35}Cl are 1.673×10^{-27} kg and 58.06×10^{-27} kg, respectively.)

Ans: The reduced mass for HCl: $\mu = \frac{m_1 m_2}{m_1 + m_2} = 1.626 \times 10^{-27}\ kg$

The internuclear distance, $r = 143\ pm = 1.43 \times 10^{-10}$ m

The moment of inertia, $I = \mu r^2 = 1.626 \times 10^{-27} \times (1.43 \times 10^{-10})^2 = 3.33 \times 10^{-47}\ kg.m^2$

The spacing between the lines,

$$2B = \frac{2*h}{8\pi^2 Ic} = \frac{2*6.626\times10^{-34} Js}{8\times(3.14)^2\times(3.33\times10^{-47}\ kg.m^2)\times(3\times10^{10}\ cm.s^{-1})} = 16.80\ cm^{-1}$$

$$2B = \frac{2h}{8\pi^2 Ic}$$

Now, after multiple choice question let us go to some problems related to rotational spectroscopy. And this is a question based on the spacing between rotational lines. So, question is given for a gaseous is HCl molecule the inter nuclear distance is found to be 143 Pico meter. If the rotational a spectrum of HCl comprises of equally distance lines, calculate the spacing between the lines. So, you have to calculate a spacing between the lines what is given is internally or distance. So, a spacing between the lines is 2B if you remember where B is equal to h by 8 pi square Ic Ic where B is in wave number unit, wave number unit.

If we want to calculate the spacing between rotational line in hertz unit then the c will not be here, spacing will always be equal to 2B only thing is the formula will differ when you are expressing the in terms of hertz, then there will be no c, but if you are expressing B in terms of centimeter inverse then you need to write h into 8 pi square Ic. So, 2B will be 2h divided by 8 pi square Ic, 2h divided by 8 pi square Ic.

So, first thing we need to know is I because h and c are constant and we know the value of h and c and h is your 6.626 into 10 to power minus 34 Joule seconds, whereas, your c is 3 into 10 by power 10 centimeter per second. So, here I have calculated B in terms of centimeter inverse unit, our wave number unit basically, and wave number unit can also be expressed as meter inverse or centimeter inverse if you are using meter inverse then we have to express c in terms of meter per second if you want answer in centimeter inverse then we have to express velocity of light in centimeter per second.

So, h and c are the constants whose values are already known, what we need to calculate is I and for I you need to know reduce mass which is mu, your mu is given by m1 m2 divided by m1 plus m2 and m1 m2 is given here this is m1, this is m2 and you can calculate the reduced mass using this formula. One thing you must keep in mind that m1 is mass of 1 molecule mass of 1 molecule or mass of 1 atom it is not mass of 1 mole of atom or molecule.

So, what does that mean is that you have to express m1 in atomic mass unit, atomic mass unit not in gram per mole. So, but if you suppose take m1 in gram per mole unit, then you need to divide that by Avogadro number that will give you mass of 1 molecule or 1 atom not 1 mole of molecule or 1 mole of atom. So, this thing you need to keep in mind and then r you need to express in meter and then you can calculate I is equal to mu r square.

So, you can calculate moment of inertia using I is equal mu r square, mu already here calculated and r is 1.43 into 10 to power minus 10 meter and so, your moment of inertia will be in kg per meter square. And once you put here in this equation, then you can get the value of 2B which will tell you about the spacing between the lines which is equal to 16.8 centimeter inverse.

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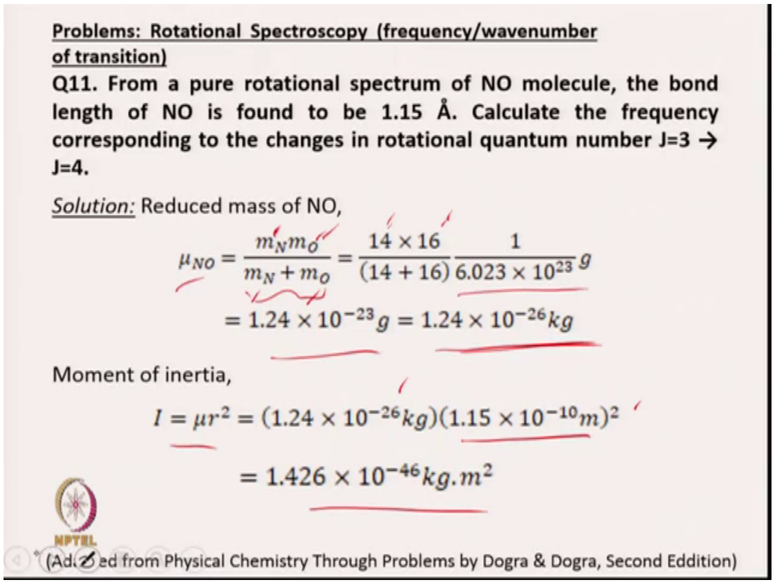


Problems: Rotational Spectroscopy (frequency/wavenumber of transition)

Q11. From a pure rotational spectrum of NO molecule, the bond length of NO is found to be 1.15 Å. Calculate the frequency corresponding to the changes in rotational quantum number J=3 → J=4.

Solution: Reduced mass of NO,

$$\mu_{NO} = \frac{m_N m_O}{m_N + m_O} = \frac{14 \times 16}{(14+16)} \frac{1}{6.023 \times 10^{23}} g$$

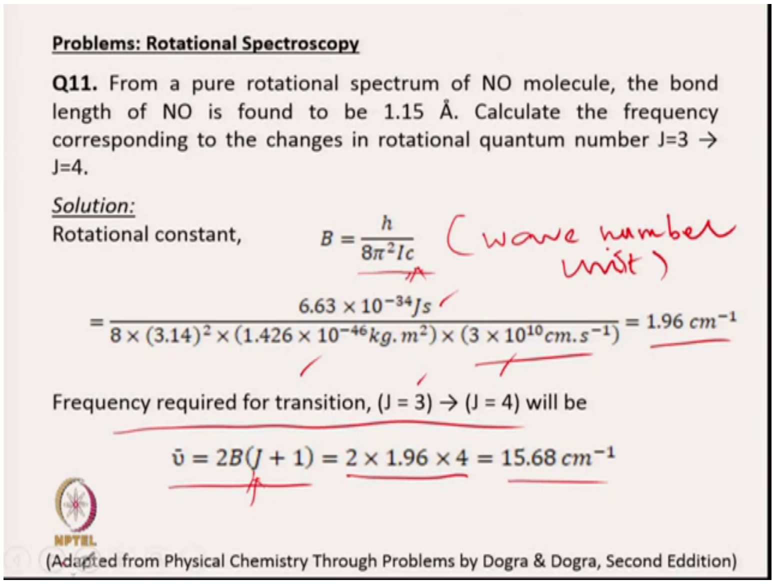
$$= 1.24 \times 10^{-23} g = 1.24 \times 10^{-26} kg$$

Moment of inertia,

$$I = \mu r^2 = (1.24 \times 10^{-26} kg)(1.15 \times 10^{-10} m)^2$$

$$= 1.426 \times 10^{-46} kg.m^2$$

(Adapted from Physical Chemistry Through Problems by Dogra & Dogra, Second Eddition)



Problems: Rotational Spectroscopy

Q11. From a pure rotational spectrum of NO molecule, the bond length of NO is found to be 1.15 Å. Calculate the frequency corresponding to the changes in rotational quantum number J=3 → J=4.

Solution:

Rotational constant, $B = \frac{h}{8\pi^2 Ic}$ (wave number unit)

$$= \frac{6.63 \times 10^{-34} Js}{8 \times (3.14)^2 \times (1.426 \times 10^{-46} kg.m^2) \times (3 \times 10^{10} cm.s^{-1})} = 1.96\, cm^{-1}$$

Frequency required for transition, (J = 3) → (J = 4) will be

$$\tilde{\upsilon} = 2B(J+1) = 2 \times 1.96 \times 4 = 15.68\, cm^{-1}$$

(Adapted from Physical Chemistry Through Problems by Dogra & Dogra, Second Eddition)

Let us go to next question in this question, you have to calculate frequency wave number of transition from the rotational spectrum. So, question is from a pure rotational spectrum of NO molecule the bond length of NO is found to be 1.15 angstrom, calculate the frequency corresponding to changes in rotational quantum number J is equal to 3 to J is equal to 4, J is equal to 3 to J is equal to 4. So, certainly we need to calculate B for that, first you need to calculate the moment of inertia and for moment of inertia we need reduced mass and bond length, bond length is already given.

So, first we need to calculate your reduced mass. So, reduced mass of NO will be given by mass of N multiplied by mass of O divided by mass of N plus mass of O, here we are taking mass of 1 nitrogen not 1 mole of nitrogen. Here you will take mass of 1 oxygen and again this is mass of 1 nitrogen plus mass of 1 oxygen. So, this is 14 and 16 divided by 14 plus 16 we now need to divide by Avogadro number, because 14 and 16 gram is basically the weight of 1 mole of nitrogen or mass of 1 mole of nitrogen and mass of 1 mole of oxygen respectively.

So, we need to divide by Avogadro number and once we divide by Avogadro number what we are going to get is your reduced mass in kg, first you will get reduced mass in grams and then you divide by 1000 you will get to this mass in kg. Now, we can calculate moment of inertia by using this equation, I equal to mu into r square, r is already given that is 1.15 angstrom and that is basically 1.15 into 10 to the power minus 10 meter.

So, you square this and multiplied by this reduced mass you will get moment of inertia in kg meter square. So, now, we know what is the moment of inertia. Now, let us go and calculate your rotational constant, rotational constant in wave number unit is your h divided by 8 pi Square Ic. So, B is equal to h divided by 8 pi Square Ic, here this is in wave number unit wave number unit, wave number unit. If we want to express B in hertz unit then we need to just remove this c, this c.

So, now, we can go ahead and calculate B since we know what is the value of h, what is the value of c and what is the value of I. So, this is your value of h, this is what we calculated and this is your velocity of light in centimeter per second and so our B will be in centimeter inverse unit if you take c in meter per second then we will get the answer in meter inverse unit and the answer is 1.96 centimeter inverse and now, we can calculate what is the frequency required for transition from J is equal 3 to J is equal to 4.

Now, again you keep in mind some sometime you write nu bar as 2BJ and in some work you will find it 2BJ plus 1, but that is not basically different because, when you express your nu bar in 2BJ, then I am talking about J value for the excited state and when I say nu bar is equal to 2B J plus 1 then the J is the value from, value of the energy level from where transition is happening, from where transition is happening. So, here the value of J is 3 and so, you can get nu bar and nu bar will be 2B into 4, B we have already calculated and so, nu bar is 15.68 centimeter inverse.

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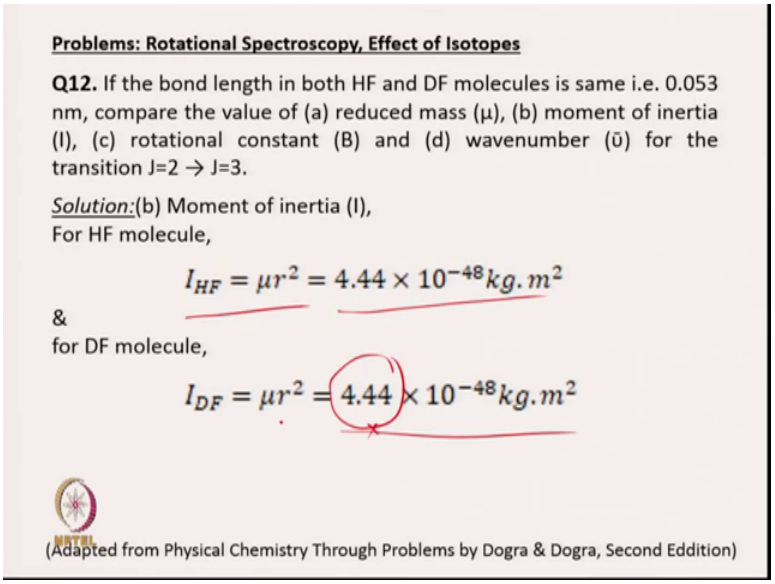


Problems: Rotational Spectroscopy, Effect of Isotopes

Q12. If the bond length in both HF and DF molecules is same i.e. 0.053 nm, compare the value of (a) reduced mass (μ), (b) moment of inertia (I), (c) rotational constant (B) and (d) wavenumber (ῡ) for the transition J=2 → J=3.

Solution:(b) Moment of inertia (I),

For HF molecule,

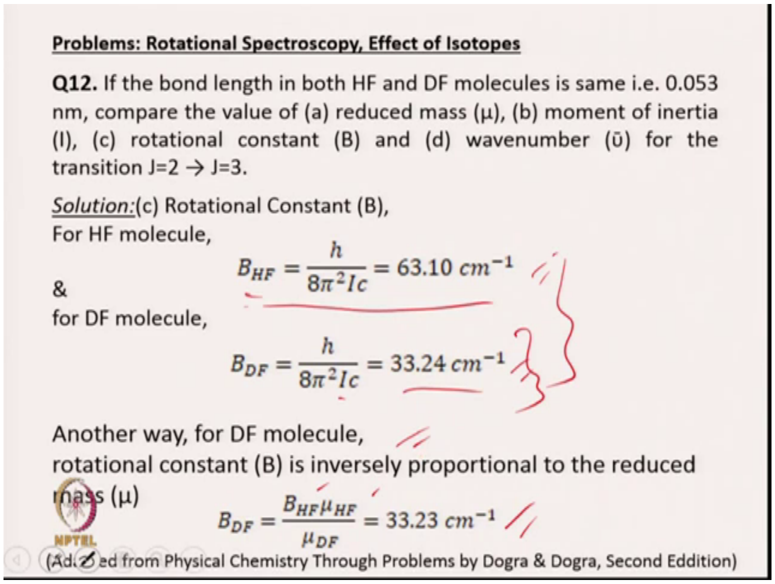
$$I_{HF} = \mu r^2 = 4.44 \times 10^{-48} kg.m^2$$

&

for DF molecule,

$$I_{DF} = \mu r^2 = 4.44 \times 10^{-48} kg.m^2$$

(Adapted from Physical Chemistry Through Problems by Dogra & Dogra, Second Eddition)



Problems: Rotational Spectroscopy, Effect of Isotopes

Q12. If the bond length in both HF and DF molecules is same i.e. 0.053 nm, compare the value of (a) reduced mass (μ), (b) moment of inertia (I), (c) rotational constant (B) and (d) wavenumber (ῡ) for the transition J=2 → J=3.

Solution:(c) Rotational Constant (B),

For HF molecule,

$$B_{HF} = \frac{h}{8\pi^2 Ic} = 63.10\ cm^{-1}$$

&

for DF molecule,

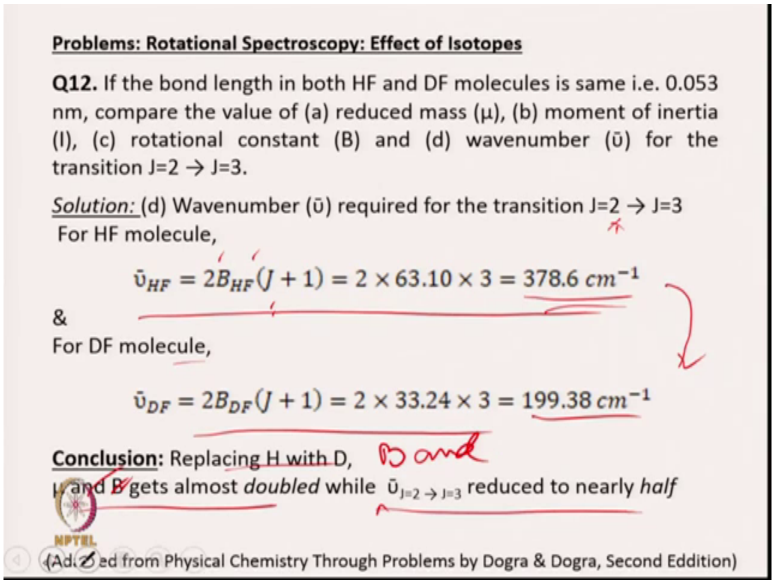
$$B_{DF} = \frac{h}{8\pi^2 Ic} = 33.24\ cm^{-1}$$

Another way, for DF molecule,

rotational constant (B) is inversely proportional to the reduced mass (μ)

$$B_{DF} = \frac{B_{HF}\mu_{HF}}{\mu_{DF}} = 33.23\ cm^{-1}$$

(Adapted from Physical Chemistry Through Problems by Dogra & Dogra, Second Eddition)



Problems: Rotational Spectroscopy: Effect of Isotopes

Q12. If the bond length in both HF and DF molecules is same i.e. 0.053 nm, compare the value of (a) reduced mass (μ), (b) moment of inertia (I), (c) rotational constant (B) and (d) wavenumber ($\bar{\upsilon}$) for the transition J=2 → J=3.

Solution: (d) Wavenumber ($\bar{\upsilon}$) required for the transition J=2 → J=3

For HF molecule,

$$\bar{\upsilon}_{HF} = 2B_{HF}(J+1) = 2 \times 63.10 \times 3 = 378.6\ cm^{-1}$$

&

For DF molecule,

$$\bar{\upsilon}_{DF} = 2B_{DF}(J+1) = 2 \times 33.24 \times 3 = 199.38\ cm^{-1}$$

Conclusion: Replacing H with D, B and

μ and ~~B~~ gets almost *doubled* while $\bar{\upsilon}_{J=2 \rightarrow J=3}$ reduced to nearly *half*

(Ad[illegible]ed from Physical Chemistry Through Problems by Dogra & Dogra, Second Eddition)

Now, next question is basically to look at the effect of isotopes, question reads as if the bond length in both HF and DF molecule is same and it is given as (0.03) 0.053 nanometer. Now, we have to compare the value of reduced mass. So, when you are going from HF to DF and bond length is same then what is the effect of isotope on reduced mass, moment of inertia, rotational constant, a wave number for the transition J is equal to 2 to J is equal to 3.

So, let us go first calculate reduced mass, mu HF will be mass of 1 hydrogen atom multiplied mass of 1 fluorine atom divided the mass of 1 hydrogen atom plus mass of 1 fluorine atom when you do the calculation, what you will get is 1.58 into 10 to power minus 27 kg. Same calculation you can do DF molecule and the answer will be 3 into 10 by power minus 27 kg and so, you can just divide mu DF by mu HF and you can see what will the value of reduced mass for these 2 molecules. If you notice it the mu DF is almost twice that of mu HF.

Now, let us go and calculate moment of inertia and moment of inertia is given by mu r square and r is taken to be constant and is equal to 0.53 nanometer when you do the appropriate substitution what you are going to get is moment of inertia in kg meter square and this is your 4.44 into 10 by power minus 48. And for DF it will be equal to I think this will be almost double of that this is wrong. So, please correct it probably this is 8.88 you do the calculation it is not very difficult why I am saying double because mu of IHF is half of mu of DF.

So, please make the appropriate correction. Now, once we know the mu value and I value we can go ahead and look at the rotational constant for these 2 molecules. And if you do a calculation for

HF, using B is equal to h by 8 pi square Ic, you will get the B value for HF equal to 63.10 centimeter inverse and B of DF is 33.24 centimeter inverse, 33.24 (centi inverse) centimeter inverse, this is right. Now you see that this rotational constant is inversely proportional to moment of inertia. And since moment of energy, of FF is twice that of HF.

And so B value will be, B value of DF will be half of the value of HF approximately half of the value of B value of HF and that is what it is it in here that by using the concept that rotational constant inversely proportional to reduced mass we can calculate the B value of DF. Since we know B value of HF. So, we may not need to calculate this, we can simply do we can simply use this formula BHF into mu HF by mu DF. So after the calculation of rotational constant for HF and DF now we will see what is the value of wave number for the transition J is equal to 2 to J is equal to 3.

So, we can use this formula to know the wave number again J is value of rotational level from where transition is happening, from where transition is happening. So, here transition is happening from J is equal to 2. So, J is equal to 2 here and so, you can calculate the 2B into J plus 1 and this is 2 into 63.1 into 3 and the answer is 378.6 centimeter inverse. For DF molecule same equation can be used and then wave number what we get for J is equal to 2 to J is equal to 3 transition is 199.38 centimeter inverse. Again you can see your nu bar DF is half of nu bar HF and that is not surprising because B of DF is half of B for HF. So, replacing H with D nu gets doubled. So, I think this is wrong nu gets doubled whereas B and nu bar reduce to nearly half.

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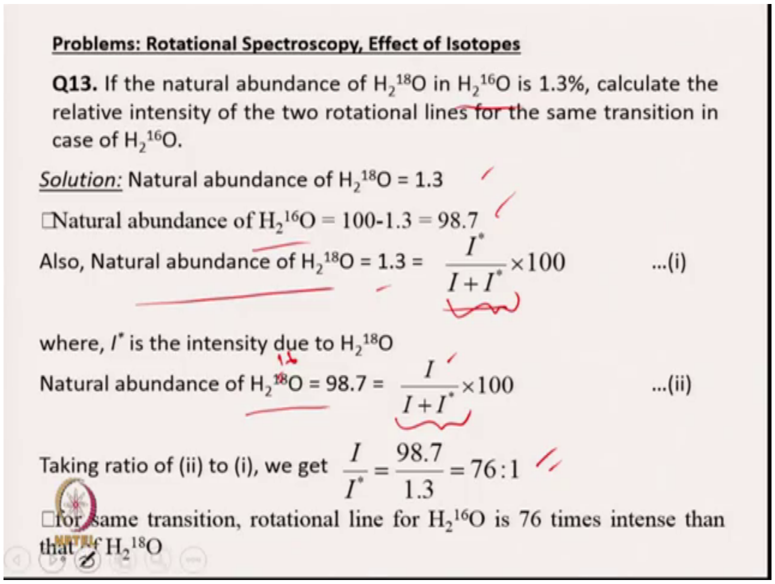

Problems: Rotational Spectroscopy, Effect of Isotopes

Q13. If the natural abundance of $H_2{}^{18}O$ in $H_2{}^{16}O$ is 1.3%, calculate the relative intensity of the two rotational lines for the same transition in case of $H_2{}^{16}O$.

Solution: Natural abundance of $H_2{}^{18}O$ = 1.3

☐Natural abundance of $H_2{}^{16}O$ = 100-1.3 = 98.7

Also, Natural abundance of $H_2{}^{18}O$ = 1.3 = $\frac{I^*}{\underbrace{I+I^*}}\times 100$ ...(i)

where, I^* is the intensity due to $H_2{}^{18}O$

Natural abundance of $H_2{}^{\overset{16}{18}}O$ = 98.7 = $\frac{I}{\underbrace{I+I^*}}\times 100$ ...(ii)

Taking ratio of (ii) to (i), we get $\frac{I}{I^*} = \frac{98.7}{1.3} = 76:1$

☐for same transition, rotational line for $H_2{}^{16}O$ is 76 times intense than that of $H_2{}^{18}O$

So, now, let us see another question based on effect of isotopes. So, question is, if the natural abundance of H2 18O in H2 16O is 1.3 percent, calculate the relative intensity of 2 rotational lines for the same transition in case of H2 16O. So, natural abundance of H2 18O is given 1.3. So, natural abundance of H2 16O can be calculated and that is 100 minus 1.3 and that in 98.7

So, natural abundance of H2 18O always 1.3 and that should be equal to intensity for this H2 18O divided by intensity for H2 16O plus intensity of H2 18O multiplied by 100. So, I star is intensity due to H2 18O and I is intensity due to H2 16O. So, natural abundance of H2 18O is equal to your 90 sorry this is 16O natural abundance of H2 16O will be equal to 98.7 and that will be equal to I divided by I plus I star into 100 and if you take the ratio of this, this I plus I star will get cancel out. So, I by I star is equal to 98.7 divided by 1.3 and that gives you 76 is to 1 so, for the same transition, rotational line for H2 16O is 76 times intense than that of H2 18O.

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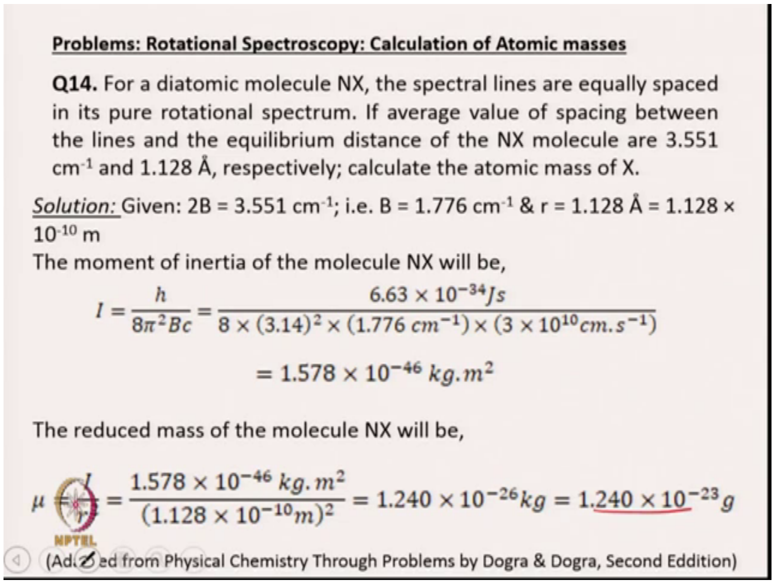


Problems: Rotational Spectroscopy: Calculation of Atomic masses

Q14. For a diatomic molecule NX, the spectral lines are equally spaced in its pure rotational spectrum. If average value of spacing between the lines and the equilibrium distance of the NX molecule are 3.551 cm^{-1} and 1.128 Å, respectively; calculate the atomic mass of X.

Solution: Given: 2B = 3.551 cm^{-1}; i.e. B = 1.776 cm^{-1} & r = 1.128 Å = 1.128 × 10^{-10} m

The moment of inertia of the molecule NX will be,

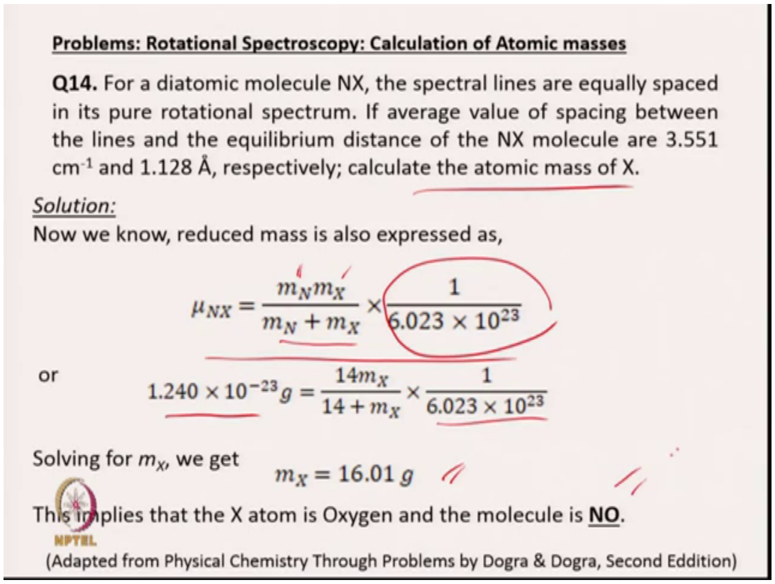
$$I = \frac{h}{8\pi^2 Bc} = \frac{6.63 \times 10^{-34} Js}{8 \times (3.14)^2 \times (1.776\ cm^{-1}) \times (3 \times 10^{10} cm.s^{-1})}$$

$$= 1.578 \times 10^{-46}\ kg.m^2$$

The reduced mass of the molecule NX will be,

$$\mu = \frac{I}{r^2} = \frac{1.578 \times 10^{-46}\ kg.m^2}{(1.128 \times 10^{-10} m)^2} = 1.240 \times 10^{-26} kg = 1.240 \times 10^{-23} g$$

(Adapted from Physical Chemistry Through Problems by Dogra & Dogra, Second Eddition)



Problems: Rotational Spectroscopy: Calculation of Atomic masses

Q14. For a diatomic molecule NX, the spectral lines are equally spaced in its pure rotational spectrum. If average value of spacing between the lines and the equilibrium distance of the NX molecule are 3.551 cm^{-1} and 1.128 Å, respectively; calculate the atomic mass of X.

Solution:

Now we know, reduced mass is also expressed as,

$$\mu_{NX} = \frac{m_N m_X}{m_N + m_X} \times \frac{1}{6.023 \times 10^{23}}$$

or

$$1.240 \times 10^{-23} g = \frac{14 m_X}{14 + m_X} \times \frac{1}{6.023 \times 10^{23}}$$

Solving for m_X, we get $m_X = 16.01\ g$

This implies that the X atom is Oxygen and the molecule is **NO**.

(Adapted from Physical Chemistry Through Problems by Dogra & Dogra, Second Eddition)

Now, next question is calculation of atomic mass. The question is for a diatomic molecule NX the spectral lines are equally a space in its pure rotational spectrum if average value of a spacing between the lines and the equilibrium distance of NX molecule 3.551 centimeter inverse and 1.1 to 8 angstrom and calculate the atomic mass of X.

So, based on rotational spectra, you can calculate the atomic masses and this is 1 of the example. So, again first we will calculate the reduced mass and reduced mass is mass of N multiplied by mass of X divided by mass of N plus mass of X into 1 divided by 6.023 into 10 to power 23. So, this we are doing because we are taking mN as molar mass So, if you take mN as molar mass then we will divide it by Avogadro number.

So, this is your mN you know that 14 into mX divided by 14 plus mX into 1 by 6.023 into 10 to power 23 and this is equal to mu obtained from let me see this mu obtained from the mu is what 1.24 into 10 to power minus 23. So, if you put it here you can calculate mX is equal to 16.01 and since mX is equal to 16.01. So, your molecule is a NO and your atom X is oxygen, atom X is oxygen.

So, the question 14 is that if you record the rotational spectrum of a molecule in which you do not know the atomic mass of one of the atom, so, here we are talking about diatomic atom, diatomic molecule and what you do is you take a rotational spectrum look at the what is the spacing between 2 lines that will give you a B from B you can know I and I will give you reduced mass if you know bond length, if you know bond length and once you know mu then you can calculate the mass of the other atom which is X here and what we showed you is that mass of the unknown atom is 16 gram and that tells you that the X atom is your oxygen atom.

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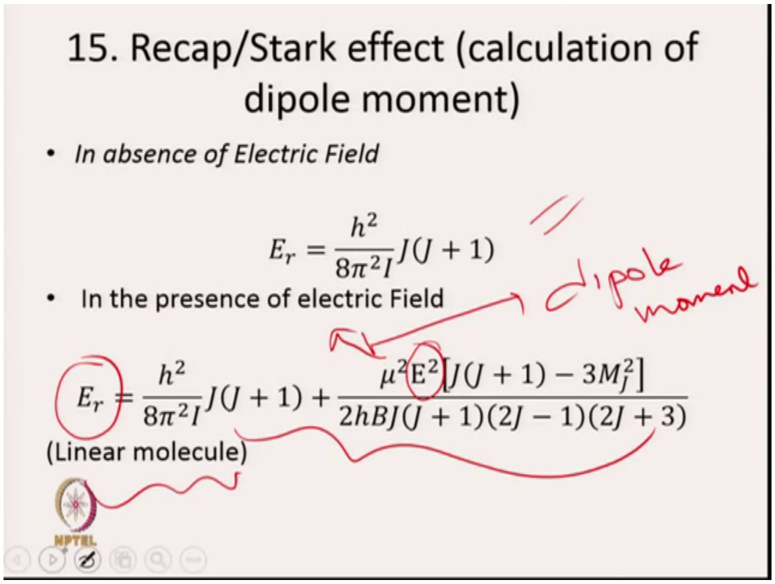


15. Recap/Stark effect (calculation of dipole moment)

- *In absence of Electric Field*

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1)$$

- In the presence of electric Field

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) + \frac{\mu^2 E^2 [J(J+1) - 3M_J^2]}{2hBJ(J+1)(2J-1)(2J+3)}$$

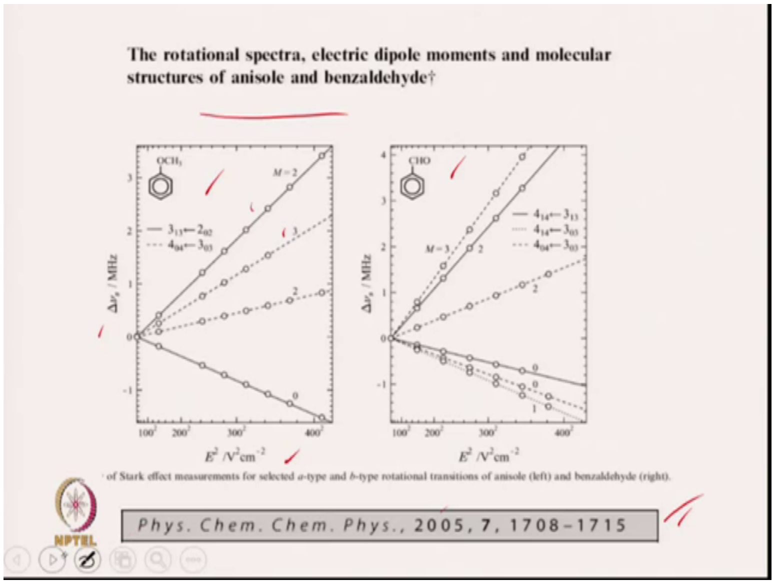
(Linear molecule)

dipole moment

Stark Shift in frequency

$$\Delta E_r = \frac{\mu^2 E^2[J(J+1)-3M_J^2]}{2hBJ(J+1)(2J-1)(2J+3)}$$

$$\Delta \nu = \frac{\mu^2 E^2[J(J+1)-3M_J^2]}{2h^2BJ(J+1)(2J-1)(2J+3)}$$



The rotational spectra, electric dipole moments and molecular structures of anisole and benzaldehyde†

of Stark effect measurements for selected *a*-type and *b*-type rotational transitions of anisole (left) and benzaldehyde (right).

Phys. Chem. Chem. Phys., 2005, 7, 1708–1715

Now, next question is calculation of dipole moment. I have not given a question, but I will show you one result from literature how to calculate dipole moment of molecule using rotational spectroscopy. So, for that, we know that in the absence of electric field, the energy of rotational levels is given by this h square by 8 pi square IJ J plus 1 and J is rotational quantum number and when you place the molecule in the electric field, then degeneracy is destroyed and in that case, for a linear molecule you give Er with this equation, Er with this equation and if I plot Er versus E square what I am going to get is mu square which is basically, here please do not confuse this mu with the reduce mass.

This one is your dipole moment, dipole moment, moment. So, if you plot Er versus E square, where is your electrical field you can get the dipole moment of a molecule, of a molecule. So, Er is basically delta Er is given by this value and then delta nu is given by this value. So, delta nu is basically delta ER by h and you can see that it is 2h square here it is 2h and when I plot delta nu vs E square, I can get the value of dipole moment where nu is your dipole moment. So, I am showing you the calculation done in our paper.

This is paper from PCCP that is published in 2005. They calculated the dipole moment of anisole and benzaldehyde. And here you see data mu versus E square. That is what we generally plot to get the dipole moment and they have calculated dipole moment, they have calculated dipole moment using this plot. Similarly, this is for anisole and this is for benzaldehyde. So, this is the way to calculate your dipole moment of a molecule using the splitting of rotational lines in electric field, electric field which is known as dark effect.

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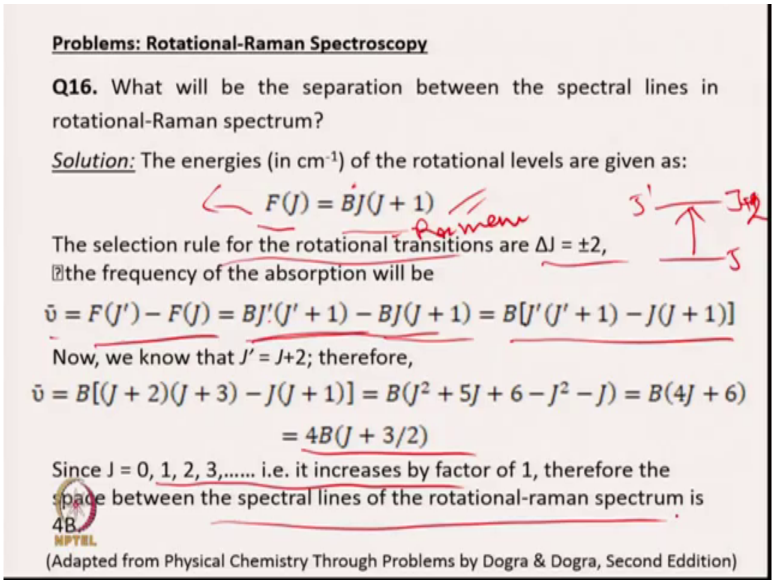

Problems: Rotational-Raman Spectroscopy

Q16. What will be the separation between the spectral lines in rotational-Raman spectrum?

Solution: The energies (in cm^{-1}) of the rotational levels are given as:

$$F(J) = BJ(J+1)$$

The selection rule for the rotational transitions are $\Delta J = \pm 2$,

⍰the frequency of the absorption will be

$$\bar{\upsilon} = F(J') - F(J) = BJ'(J'+1) - BJ(J+1) = B[J'(J'+1) - J(J+1)]$$

Now, we know that $J' = J+2$; therefore,

$$\bar{\upsilon} = B[(J+2)(J+3) - J(J+1)] = B(J^2 + 5J + 6 - J^2 - J) = B(4J+6)$$

$$= 4B(J + 3/2)$$

Since J = 0, 1, 2, 3,...... i.e. it increases by factor of 1, therefore the space between the spectral lines of the rotational-raman spectrum is 4B.

(Adapted from Physical Chemistry Through Problems by Dogra & Dogra, Second Eddition)

Now, next question is from rotational Raman spectroscopy. So, what is the separation between spectral lines and rotational Raman spectrum, we know the separation between a spectral lines in rotational spectrum and that is equal 2B. Now we are going to see what is the separation between spectral lines in rotational Raman spectrum. So, this is your energy of the rotational levels FJ is equal to BJ J plus 1. Now, if you take if in hertz unit, then B will be in hertz and if you take F in centimeter inverse unit then B will be in centimeter inverse.

So, this F is given by BJ J plus 1 and let us take this in centimeter inverse and B is in centimeter inverse. Now, selection rule for rotational transition, rotational Raman transition or delta J is equal to plus minus 2 that I have already discuss. So, let us calculate nu bar, nu bar is your wave number for transition between J to J plus 1 level J to J plus 1 level. So, that is given by FJ dash this is let us take this as a J dash, so FJ dash minus FJ.

And if you take J dash for J dash, you can write BJ dash J dash plus 1 minus BJ J plus 1. And J dash will be J plus 2 because your selection rule for rotational transition delta J is equal to plus minus 2. So, your nu bar is B J dash J dash plus 1 minus B J J plus 1. And if you take B out, this is the expression and we know that J dash is equal to J plus 2 because that is what the selection rule for rotational Raman transition. So that is right rotational Raman, Raman transition.

And so, nu bar is equal to BJ plus 2 for J dash you put J plus 2 J dash plus 1 J plus 3 minus J J plus 1 and what you get in this equation 4B J plus 3 by 2 J plus 3 by 2. So since J is equal to 0, 1, 2, 3. So, J increases by 1 and so spacing between spectral lines of rotational Raman spectrum is 4B. So, the separation between spectrum lines and rotational spectrum is 2B whereas separation between spectral lines in rotational Raman spectrum is 4B.

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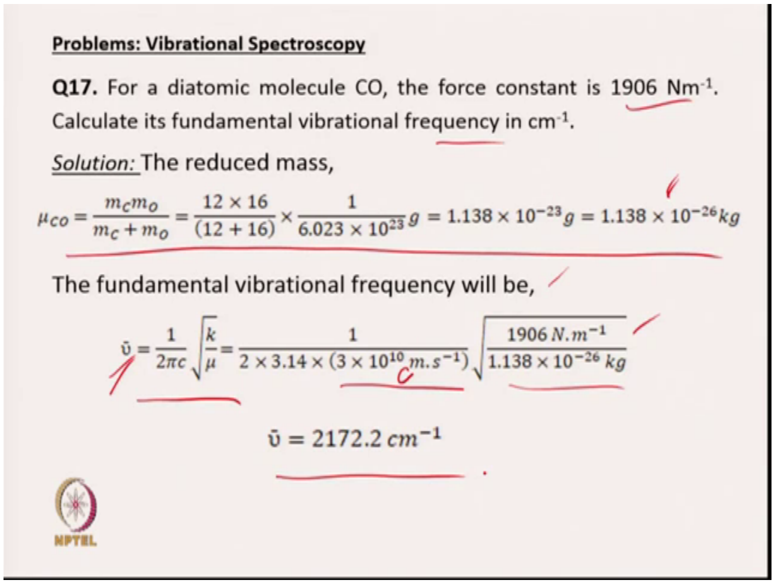

Problems: Vibrational Spectroscopy

Q17. For a diatomic molecule CO, the force constant is 1906 Nm^{-1}. Calculate its fundamental vibrational frequency in cm^{-1}.

Solution: The reduced mass,

$$\mu_{co} = \frac{m_c m_o}{m_c + m_o} = \frac{12 \times 16}{(12+16)} \times \frac{1}{6.023 \times 10^{23}} g = 1.138 \times 10^{-23} g = 1.138 \times 10^{-26} kg$$

The fundamental vibrational frequency will be,

$$\bar{\upsilon} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = \frac{1}{2 \times 3.14 \times (3 \times 10^{10} \underset{c}{} m.s^{-1})}\sqrt{\frac{1906\, N.m^{-1}}{1.138 \times 10^{-26}\, kg}}$$

$$\bar{\upsilon} = 2172.2\, cm^{-1}$$

Now, next question is based on vibrational spectroscopy for a diatomic molecules CO the force constant is 1906 Newton per meter. So, you need to calculate what is the fundamental vibrational frequency in a centimeter inverse. Again first we have to calculate mu. I have discussed calculation of mu several times so, I am not going to discuss it again. The value which you obtained from mu for CO molecule is 1.138 in 10 to the power minus 26 kg.

So fundamental frequency will be nu bar is 1 by 2 pi c, root k by mu again the wave number can be so this is wave number, so it will be in meter inverse or centimeter inverse unit. So, just put the values 1 by 2 pi c is your 3 into 10 to power 10 centimeter per second inverse. So, please correct this is a centimeter per second inverse and this is your k which is force constant it is given 1906 Newton per meter and this is your reduced mass which we just calculated for CO molecule and what will you get is wave number to be 2172.2 centimeter inverse.

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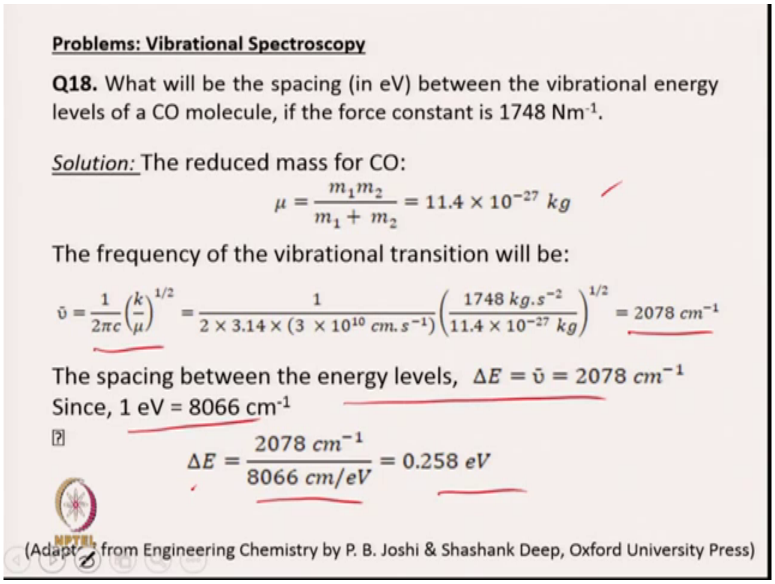

Problems: Vibrational Spectroscopy

Q18. What will be the spacing (in eV) between the vibrational energy levels of a CO molecule, if the force constant is 1748 Nm^{-1}.

Solution: The reduced mass for CO:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = 11.4 \times 10^{-27}\ kg$$

The frequency of the vibrational transition will be:

$$\bar{\upsilon} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} = \frac{1}{2 \times 3.14 \times (3 \times 10^{10}\ cm.s^{-1})}\left(\frac{1748\ kg.s^{-2}}{11.4 \times 10^{-27}\ kg}\right)^{1/2} = 2078\ cm^{-1}$$

The spacing between the energy levels, $\Delta E = \bar{\upsilon} = 2078\ cm^{-1}$

Since, 1 eV = 8066 cm^{-1}

⍰

$$\Delta E = \frac{2078\ cm^{-1}}{8066\ cm/eV} = 0.258\ eV$$

(Adapt from Engineering Chemistry by P. B. Joshi & Shashank Deep, Oxford University Press)

Now, next question is what will be the spacing in electron volt between vibrational energy level of a CO molecule if the force constant is 1748 Newton per meter. Now we are going to calculate the frequency of vibrational transition. Again we will calculate mu, mu just be calculated for CO, this is 11.4 into 10 to power minus 27 kg. So, frequency of the vibrational transition is this formula we have already discussed and that equal to 2078 centimeter inverse or 2078 centimeter inverse and this we can convert into delta E, delta E and your nu bar is related by this equation 1 electron volt is equal to 8066 centimeter inverse and so delta E can be calculated by dividing 2078 with 8066 centimeter by electron volt and what you are going to get a 0.258 electron volts. So, this is your spacing between the vibrational levels of CO molecule.

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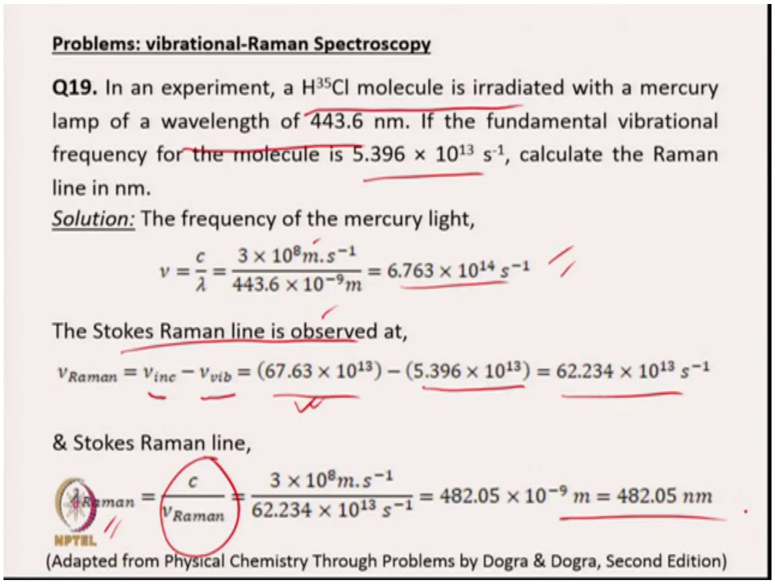

Problems: vibrational-Raman Spectroscopy

Q19. In an experiment, a $H^{35}Cl$ molecule is irradiated with a mercury lamp of a wavelength of 443.6 nm. If the fundamental vibrational frequency for the molecule is $5.396 \times 10^{13}\ s^{-1}$, calculate the Raman line in nm.

Solution: The frequency of the mercury light,

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^{8} m.s^{-1}}{443.6 \times 10^{-9} m} = 6.763 \times 10^{14}\ s^{-1}$$

The Stokes Raman line is observed at,

$$\nu_{Raman} = \nu_{inc} - \nu_{vib} = (67.63 \times 10^{13}) - (5.396 \times 10^{13}) = 62.234 \times 10^{13}\ s^{-1}$$

& Stokes Raman line,

$$\lambda_{Raman} = \frac{c}{\nu_{Raman}} = \frac{3 \times 10^{8} m.s^{-1}}{62.234 \times 10^{13}\ s^{-1}} = 482.05 \times 10^{-9}\ m = 482.05\ nm$$

(Adapted from Physical Chemistry Through Problems by Dogra & Dogra, Second Edition)

Now next question in this 35 Cl molecule is a 35 Cl molecule is irradiated with mercury lamp of a wavelength of 443.6 nanometer. If the fundamental vibrational frequency for the molecule is this second inverse what we need to calculate is what is the Raman line in nanometer. Stokes Raman line. The frequency of mercury light can be calculated using this formula nu is equal to c by lambda c again we have taken in meter per second and you can express lambda in meter and then we can get frequency in second inverse frequency in second inverse and so stokes line will be observed at nu frequency of incident light minus frequency of vibration.

Here it is a fundamental vibrational frequency we have just calculated what is the frequency of incident light and that is 67.63 into 10 to power 13 second inverse and then fundamental frequency is given. So, you just subtract this from frequency of incident light and you can get frequency of the stokes Raman line and that is equal to 62.234 into 10 to power 13 second inverse and you can also calculate wavelength of Raman by using this we know that frequency and wavelength is related by this equation c by nu and so you can calculate what will be the wavelength of stokes line, Raman line, stokes Raman line.

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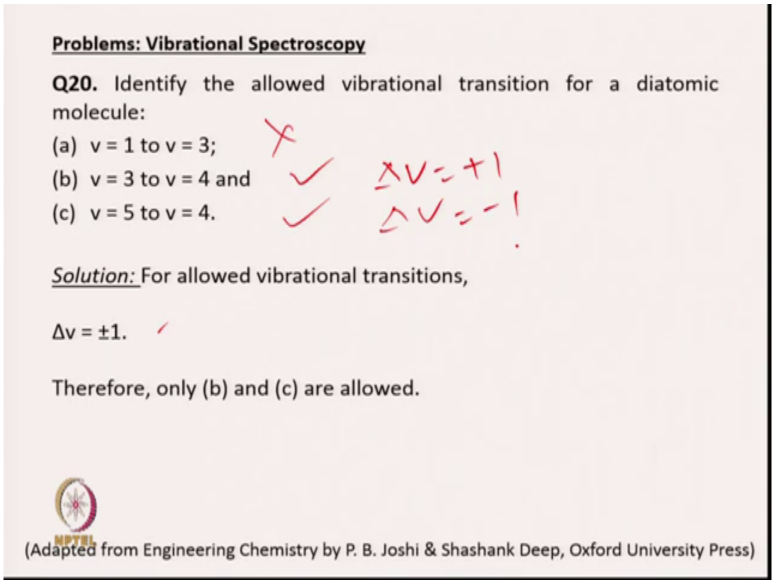

Problems: Vibrational Spectroscopy

Q20. Identify the allowed vibrational transition for a diatomic molecule:

(a) v = 1 to v = 3; ✗

(b) v = 3 to v = 4 and ✓ $\Delta v = +1$

(c) v = 5 to v = 4. ✓ $\Delta v = -1$

Solution: For allowed vibrational transitions,

$\Delta v = \pm 1$.

Therefore, only (b) and (c) are allowed.

(Adapted from Engineering Chemistry by P. B. Joshi & Shashank Deep, Oxford University Press)

So, next question is, identify the allowed vibrational transition for a diatomic molecule and again this is based on selection rules. So, you know that for allowed vibrational transmission delta v is plus minus 1 and so, first is not allowed, second is allowed, third is allowed. In the b it is delta v is equal to plus 1 and here delta v equal to minus 1.

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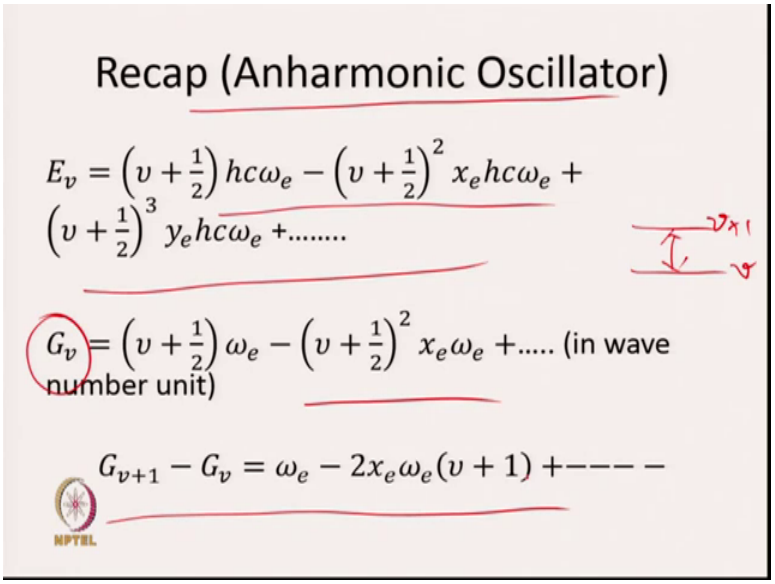
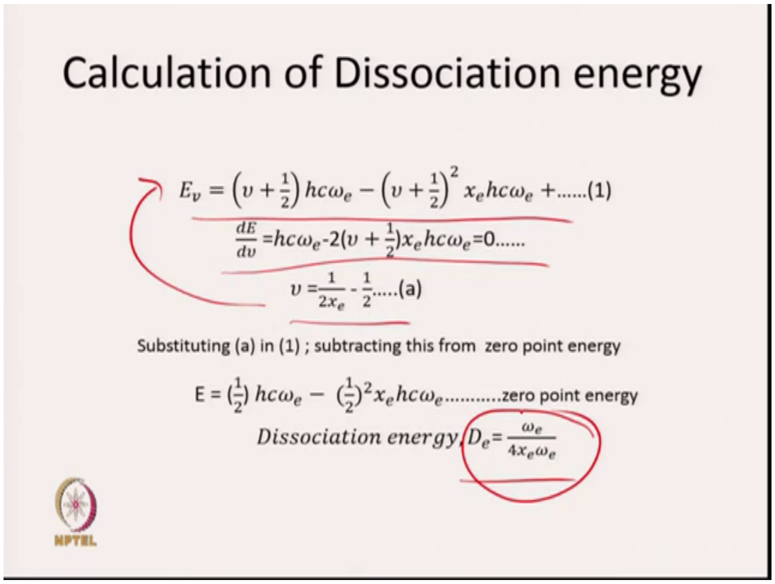


Recap (Anharmonic Oscillator)

$$E_v = \left(v+\frac{1}{2}\right)hc\omega_e - \left(v+\frac{1}{2}\right)^2 x_e hc\omega_e + \left(v+\frac{1}{2}\right)^3 y_e hc\omega_e + \ldots\ldots$$

$$G_v = \left(v+\frac{1}{2}\right)\omega_e - \left(v+\frac{1}{2}\right)^2 x_e\omega_e + \ldots\ldots \text{ (in wave number unit)}$$

$$G_{v+1} - G_v = \omega_e - 2x_e\omega_e(v+1) + - - - - -$$



Calculation of Dissociation energy

$$E_v = \left(v+\frac{1}{2}\right)hc\omega_e - \left(v+\frac{1}{2}\right)^2 x_e hc\omega_e + \ldots\ldots(1)$$

$$\frac{dE}{dv} = hc\omega_e - 2\left(v+\frac{1}{2}\right)x_e hc\omega_e = 0\ldots\ldots$$

$$v = \frac{1}{2x_e} - \frac{1}{2}\ldots\ldots(a)$$

Substituting (a) in (1) ; subtracting this from zero point energy

$$E = \left(\frac{1}{2}\right)hc\omega_e - \left(\frac{1}{2}\right)^2 x_e hc\omega_e \ldots\ldots\ldots\ldots \text{zero point energy}$$

$$\textit{Dissociation energy},\ D_e = \frac{\omega_e}{4x_e\omega_e}$$

So, next question is basically to calculate dissociation energy using vibrational spectroscopy. Just before going to discuss that question, I will like to have recap for Anharmonic oscillator, so energy of vibrational levels for anharmonic oscillator is given by this equation where v is vibrational quantum number and if you try to express this in wave number unit you need to divide by hc and that is generally given by this symbol Gv and that is basically v plus half omega e minus higher wave number turn.

So, now, you have wave number you can calculate the difference between 2 in wave number unit and when you 2 vibrational level from v to v plus 1 So, if you calculate the difference between this vibrational level centimeter inverse, you are going to get this formula. So, Gv plus 1 minus Gv is equal to omega e minus 2 Xe omega v plus 1. And so, if we plot this vs v plus 1 then we can get Xe and omega e, xe and omega e.

And now, let us think of how to calculate the vibrational level with maximum energy. And if I want to calculate the vibrational level at which energy is maximum, then I need to differentiate that and put that equal to 0 when you do that, you will get to v equal to 1 by to Xe minus half. And if you put this in this equation and then your subtract by zero point energy, what you are going to get a D. This I have explained in detail in the last lecture in the last lecture, I have explained this in detail, but what I showed you that De equal to omega e (minus) divided by 4 Xe omega e.

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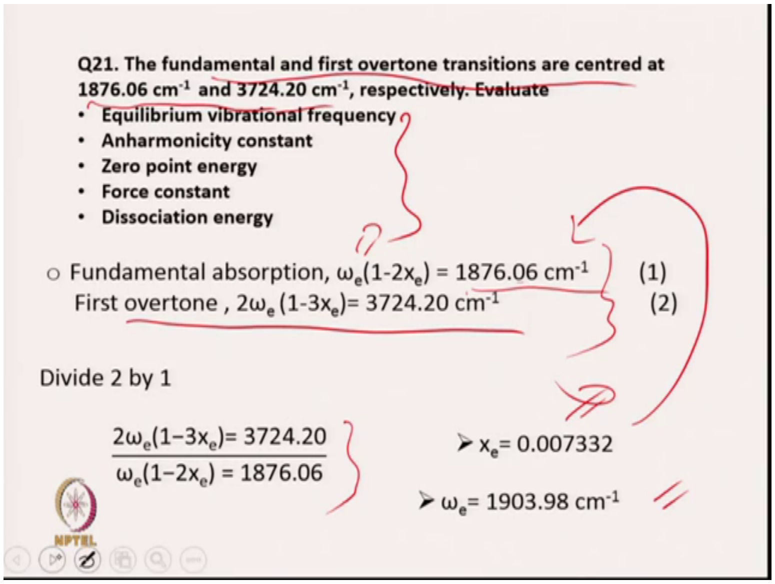


Q21. The fundamental and first overtone transitions are centred at $1876.06\ cm^{-1}$ and $3724.20\ cm^{-1}$, respectively. Evaluate

- **Equilibrium vibrational frequency**
- **Anharmonicity constant**
- **Zero point energy**
- **Force constant**
- **Dissociation energy**

○ Fundamental absorption, $\omega_e(1-2x_e) = 1876.06\ cm^{-1}$ (1)

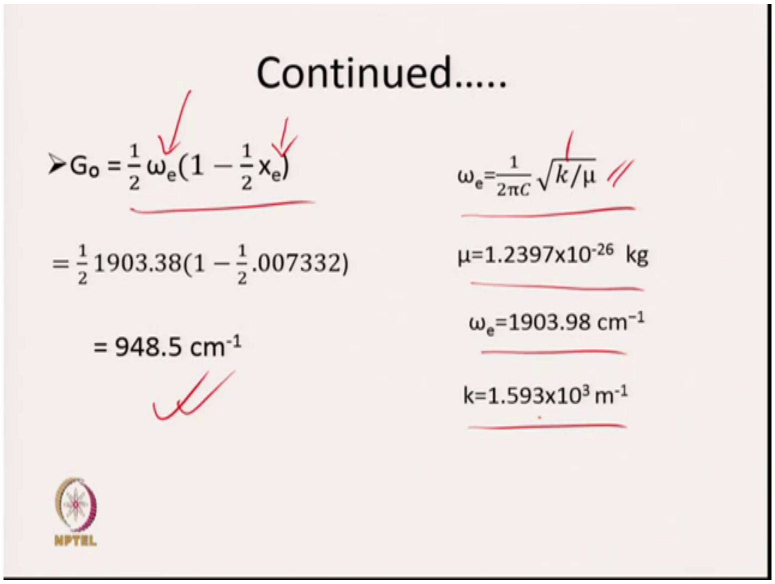
First overtone , $2\omega_e(1-3x_e) = 3724.20\ cm^{-1}$ (2)

Divide 2 by 1

$$\frac{2\omega_e(1-3x_e) = 3724.20}{\omega_e(1-2x_e) = 1876.06}$$

➢ $x_e = 0.007332$

➢ $\omega_e = 1903.98\ cm^{-1}$



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➢ $$G_0 = \frac{1}{2}\omega_e\left(1-\frac{1}{2}x_e\right)$$

$$= \frac{1}{2}1903.38\left(1-\frac{1}{2}.007332\right)$$

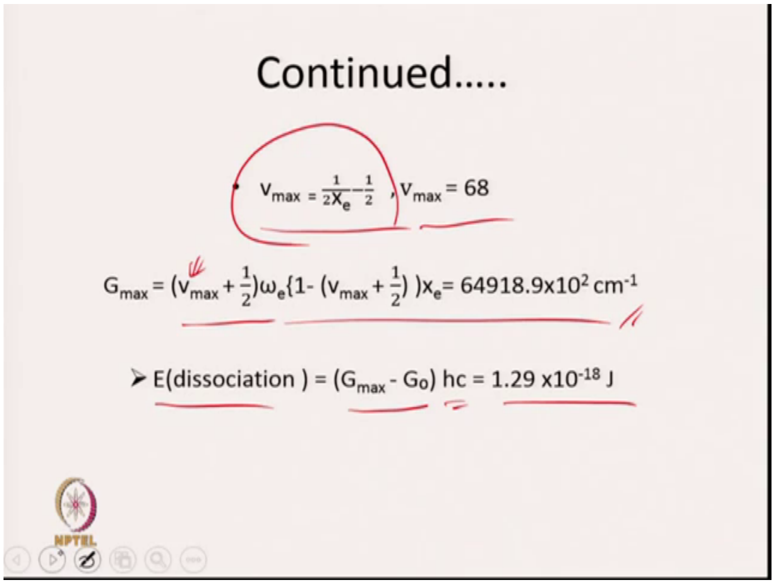
$$= 948.5\ cm^{-1}$$

$$\omega_e = \frac{1}{2\pi C}\sqrt{k/\mu}$$

$\mu = 1.2397 \times 10^{-26}$ kg

$\omega_e = 1903.98\ cm^{-1}$

$k = 1.593 \times 10^{3}\ m^{-1}$



Continued.....

$v_{max} = \frac{1}{2X_e} - \frac{1}{2}$, $v_{max} = 68$

$G_{max} = (v_{max} + \frac{1}{2})\omega_e\{1- (v_{max} + \frac{1}{2})\}x_e = 64918.9\times10^2\ cm^{-1}$

- E(dissociation) = $(G_{max} - G_0)\,hc = 1.29 \times10^{-18}$ J

So, after this recap, let us see, this question. The question is a fundamental and first overtone transition are centered at 1876.06 centimeter inverse and 3724.20 centimeter inverse respectively, and you have to calculate these 5 parameters. So, let us first start with fundamental absorption, fundamental absorption frequency is given by a wave number is given by this omega e multiplied by 1 minus 2 Xe and that is given 1876.06 centimeter inverse and for first overtone wave number is given by this equation.

So, for first overtone wave number is equal to 2 omega e multiplied by 1 minus 3 Xe. So, you have this 2. And so, you have 2 equations, and 2 unknowns, unknowns are omega e and Xe. So, you can solve these 2 equation to get the value of omega e and Xe easiest way to do is divide 1 by 2, and when you divide 1 by 2, you can get the value of Xe and when you put Xe in one of the equation and you can get value of omega e.

So, it is simple calculation you can do it easily so, please do it. Now, once you know that, what is the value of omega e and Xe, you can calculate G0 which is basically zero point energy and the zero point energy is given by this equation, this equation has already been discussed in the last lectures, last 2 lectures, so, please just go and see these equations. So, what now I do is I just plug in the value of omega e and Xe, which I obtained in the previous slide.

And when you do that, you will get the value of G naught which is basically the zero point energy. Now, you can use omega e to get the value of k basically you have to calculate k because you know mu, reduced mass is known, so reduced mass is basically this and omega e we have already obtained so we can get the value of force constant. So, if you remember the question, the fourth point is to calculate force constant. And that is what we are calculating and force constant is 1.593 into 10 to power 3 beta inverse.

Now, we need to calculate your dissociation energy for that, I told that first you have to calculate the vibrational level with maximum energy. So, you need to find out the value of v at which the energy is maximum and this is a formula for V max. And once you solve that, you will get V max equal to 68. Now, we will put the value of V max in the equation for GV when we do that will get G max. So, G max is V max plus half omega e and 1 minus V max half Xe.

And when you solve this, you will get the value of G max that the energy of the vibrational level whose energy is maximum and it is given in centimeter inverse. And you can calculate E dissociation, E dissociation is basically G max minus G0 into hc, hc is multiplied since, this the G value is in centimeter inverse. So, if you multiplied by hc then you can get the energy in joule unit, in joule unit. So, this is your dissociation energy in joule.

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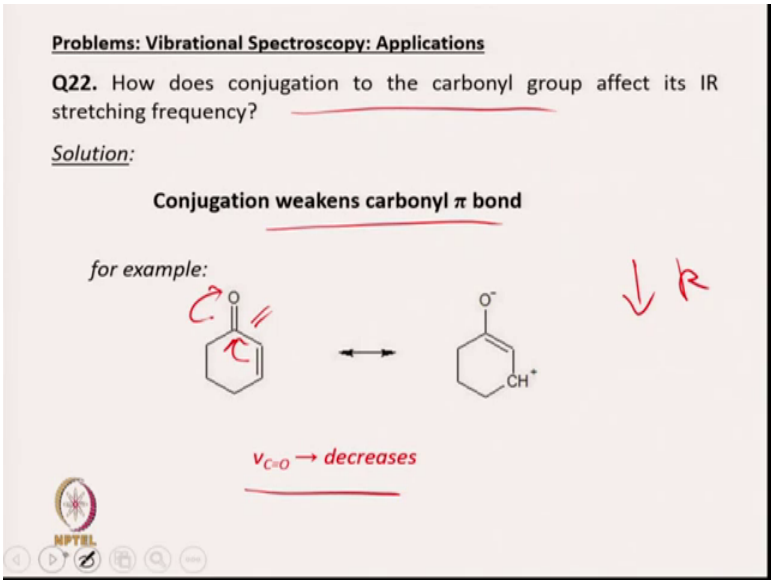

Problems: Vibrational Spectroscopy: Applications

Q22. How does conjugation to the carbonyl group affect its IR stretching frequency?

Solution:

Conjugation weakens carbonyl π bond

for example:

$\nu_{C=O}$ → *decreases*

Now, let us go to some application based questions particularly in vibrational spectroscopy. So, here first question is how does conjugation to the carbonyl group affects its IR stretching frequency? Conjugation weakens the carbonyl pi bond. So, you can see that if we look at the resonance, so, this will get a double bond and that will get a partial single bond. So, conjugation leads to weakening in carbonyl pi bond and that decreases the value of k, decreases the value of k and so, frequency of CO bond decreases. So, on conjugation frequency of CO bond decreases.

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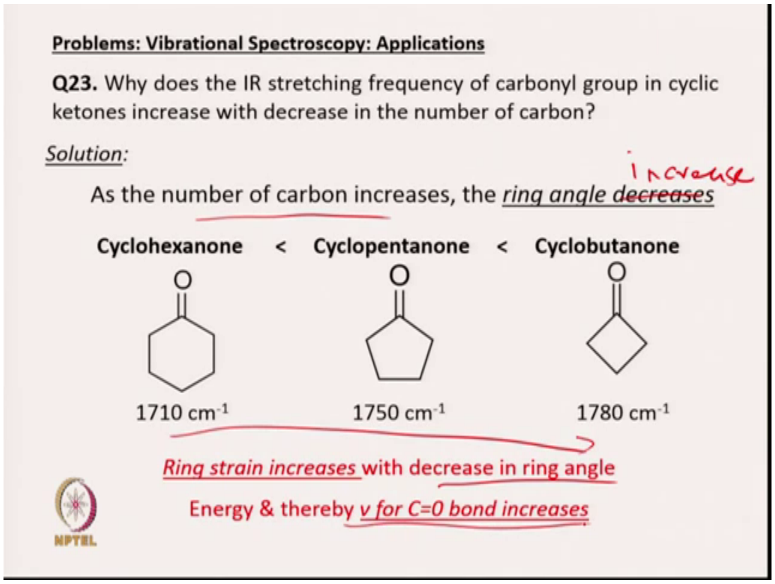

Problems: Vibrational Spectroscopy: Applications

Q23. Why does the IR stretching frequency of carbonyl group in cyclic ketones increase with decrease in the number of carbon?

Solution:

As the number of carbon increases, the *ring angle ~~decreases~~* increase

Cyclohexanone < Cyclopentanone < Cyclobutanone

1710 cm^{-1} 1750 cm^{-1} 1780 cm^{-1}

Ring strain increases with decrease in ring angle

Energy & thereby *ν for C=O bond increases*

Now, we will look at how does IR stretching frequency of carbonyl group in cyclic ketone increase with a decrease in number of carbon. So, what happens that when number of carbon in cycle increases, then ring ring angle decreases and that affects the frequency. The ring strain increases with decrease in ring angle. So, here there should be increase. So, as the number of carbon increases, ring angle increase, so, if I going from this to this side, here ring, ring angle decreases and once ring angle decreases, ring strain increases with decrease in ring angle and so energy and thereby nu for CO bond increases.

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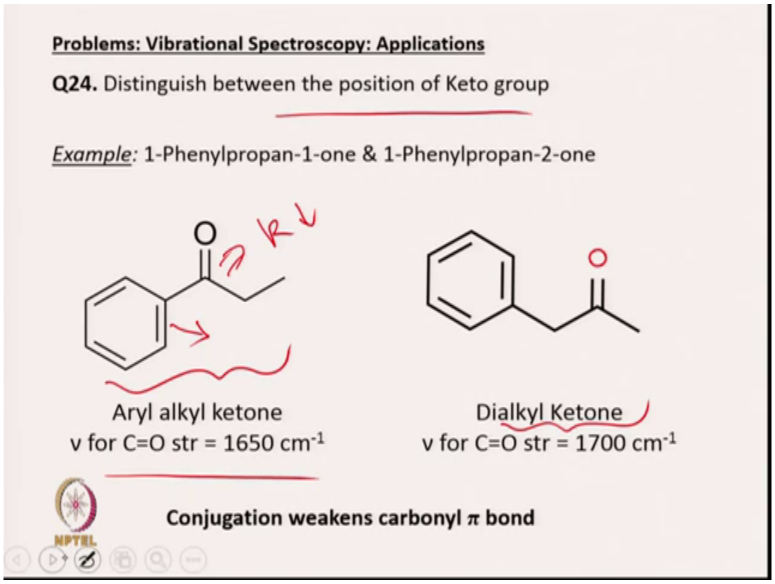

Problems: Vibrational Spectroscopy: Applications

Q24. Distinguish between the position of Keto group

Example: 1-Phenylpropan-1-one & 1-Phenylpropan-2-one

Aryl alkyl ketone

v for C=O str = 1650 cm^{-1}

Dialkyl Ketone

v for C=O str = 1700 cm^{-1}

Conjugation weakens carbonyl π bond

So, in this question what we are going to look at can we apply vibrational spectroscopy to distinguish between position of keto group, position of keto group. So, here if aryl alkyl ketone and dialkyl ketone. So, now you see that this one is involved in conjugation with the ring, benzene ring and we know that, on conjugation this k decreases and if k decreases your frequency will also decrease. and so frequency of CO stretching in aryl alkyl ketone comes at smaller wave number in comparison to dialkyl ketone. So, conjugation weakens the carbonyl pi bond.

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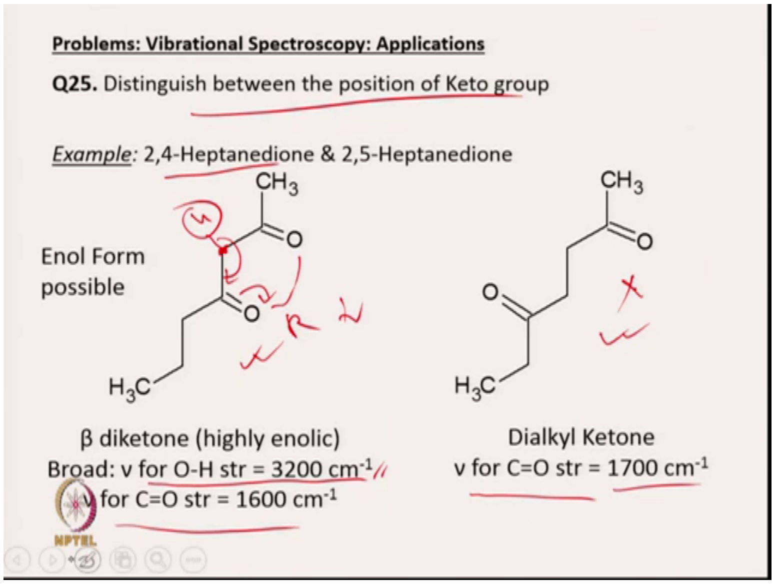

Problems: Vibrational Spectroscopy: Applications

Q25. Distinguish between the position of Keto group

Example: 2,4-Heptanedione & 2,5-Heptanedione

Enol Form possible

β diketone (highly enolic)
Broad: ν for O-H str = 3200 cm^{-1}
ν for C=O str = 1600 cm^{-1}

Dialkyl Ketone
ν for C=O str = 1700 cm^{-1}

Now, again we will see another example, we want to distinguish between the position of keto group and this is your 2,4 heptanedione, this is a 2,4 heptanedione and this is 2,5 heptanedione. Can we distinguish between these two? So, here you see, this is, this CH is basically between 2 CO group, so, here h is acidic and so, this can exist in all forms, this can exist in all forms, and if it exists in all forms what will happen is you will have a peak for OH stretching which will come around 3200 centimeter inverse and your frequency for CO will be at smaller value because your k for CO will be small. Whereas this conjugation, this enol formation is not possible in this structure. And so your nu for CO will be at 1700 centimeter inverse and there will be no peak for OH stretching, no peak for OH stretching.

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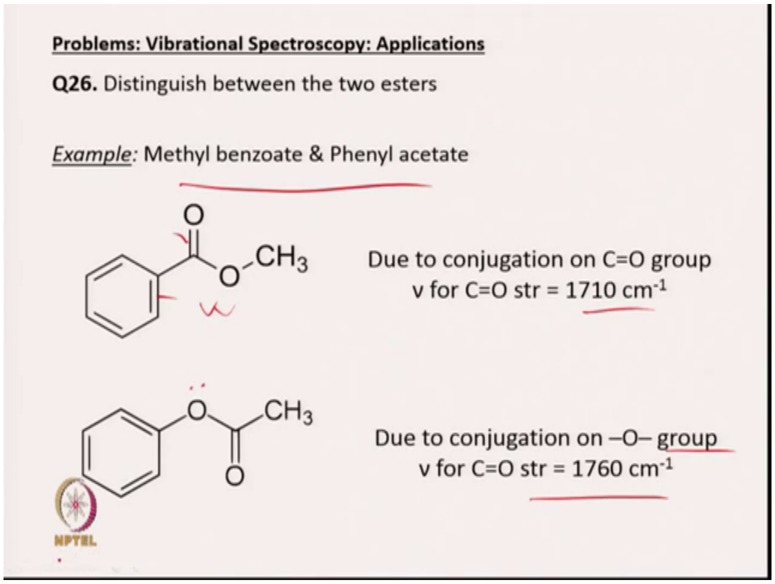

Problems: Vibrational Spectroscopy: Applications

Q26. Distinguish between the two esters

Example: Methyl benzoate & Phenyl acetate

Due to conjugation on C=O group
v for C=O str = 1710 cm^{-1}

Due to conjugation on –O– group
v for C=O str = 1760 cm^{-1}

So, now, next question is can we distinguish 2 esters the example is methyl benzoate and phenyl acetate and now you see that here the reconjugation between these two bond and in this there is conjugation with the lone pair. So, due to conjugation on O group here frequency will be 1760 centimeter inverse whereas nu for CO stretching in the above case will be at 1710 centimeter inverse.

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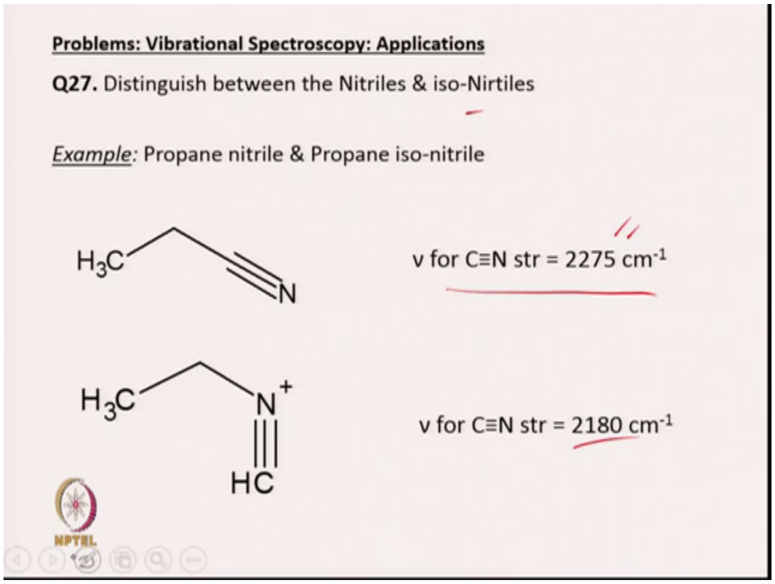

Problems: Vibrational Spectroscopy: Applications

Q27. Distinguish between the Nitriles & iso-Nirtiles

Example: Propane nitrile & Propane iso-nitrile

v for C≡N str = 2275 cm^{-1}

v for C≡N str = 2180 cm^{-1}

We can also distinguish between nitrile and iso-nitrile using vibrational spectroscopy for nitrile compound, the frequency for C triple bond N stretching will be at 2275 centimeter inverse.

Whereas, nu for this iso-nitrile will be at 2180 centimeter inverse. So, using that you can distinguish between nitrile and iso-nitrile

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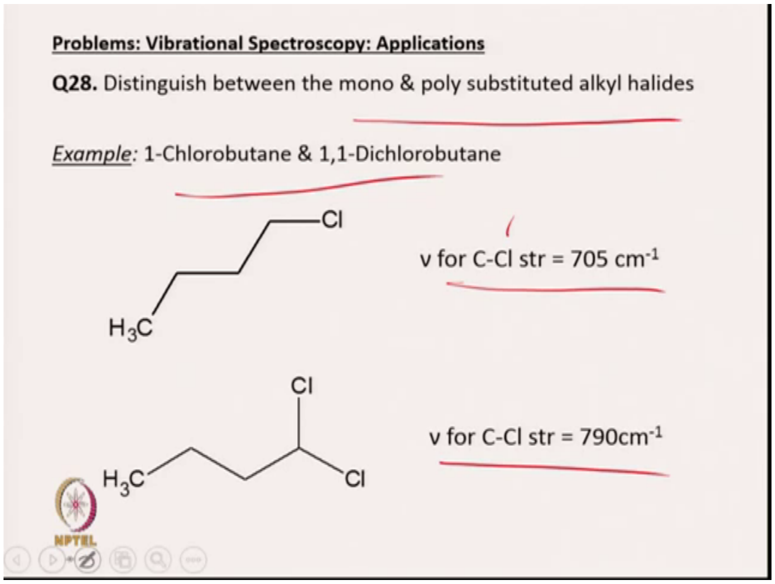

Problems: Vibrational Spectroscopy: Applications

Q28. Distinguish between the mono & poly substituted alkyl halides

Example: 1-Chlorobutane & 1,1-Dichlorobutane

v for C-Cl str = 705 cm^{-1}

v for C-Cl str = 790cm^{-1}

Mono and polyalkylated poly substituted alkyl halide, mono and poly substituted alkyl halide can also be distinguished. For example, the for example, 1 chloro butane and 1, 1 dichloro butane can be distinguished by IRS spectroscopy, here frequency will be a lower wave number when you have only one Cl, but if you have 2 Cl then this frequency will increase to 790 centimeter inverse. So, you will be able to distinguish between mono and poly substituted alkyl halide.

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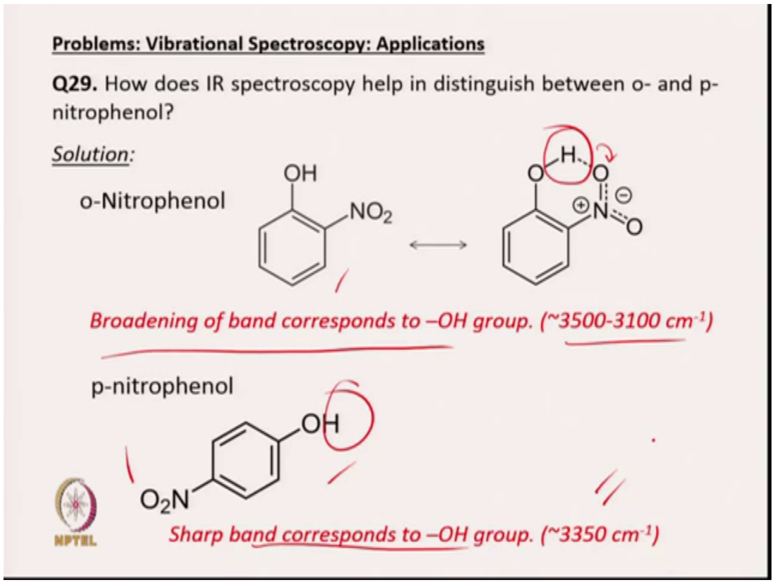

Problems: Vibrational Spectroscopy: Applications

Q29. How does IR spectroscopy help in distinguish between o- and p-nitrophenol?

Solution:

o-Nitrophenol

Broadening of band corresponds to –OH group. (~3500-3100 cm⁻¹)

p-nitrophenol

Sharp band corresponds to –OH group. (~3350 cm⁻¹)

So, next question is how we can use IRS spectroscopy to distinguish between ortho and para-nitrophenol. So, you know that in ortho-nitrophenol the hydrogen of OH group in phenol is in hydrogen bond with nitro group and that basically leads to broadening of band. So, wherever there is a hydrogen bond of OH group there will be a broadening and this broadening will be observed between 3500 to 3100 centimeter inverse. In para-nitrophenol the hydrogen bonding is not possible between this hydrogen and this nitro group and so you will get a sharp band corresponding to OH group at 3350 centimeter inverse. So, ortho and para-nitrophenol can be distinguished using IRS spectroscopy.

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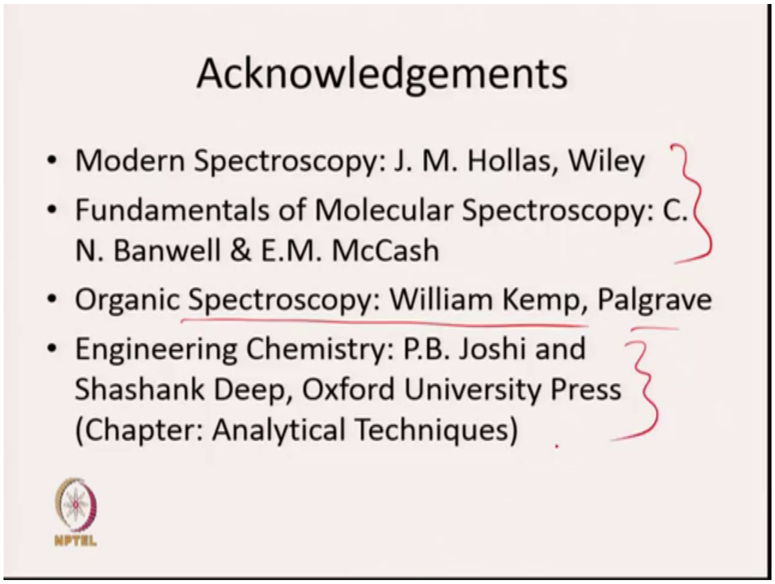

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So, in this lecture, I have looked at several different kinds of questions, some are multiple choice questions and some are problem based questions and some is application related question. So, there are a lot of different kind of application we can think of between rotational applications of rotational and vibrational spectroscopy and in the next lecture I will start with our atomic spectroscopy.

So, thank you very much for listening. Now books, I have already told you which books, I am using it, for example, in organic spectroscopy. I am taking help of William Kemp, Kemp book on organic spectroscopy, which is from Palgrave publication, and these two are for physical spectroscopy. And this is one basic books, book on your chemistry, basic book on chemistry. Thank you very much. And thank you for listening.