Fundamentals of Spectroscopy

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Lecture 39
Rotational Raman Spectroscopy

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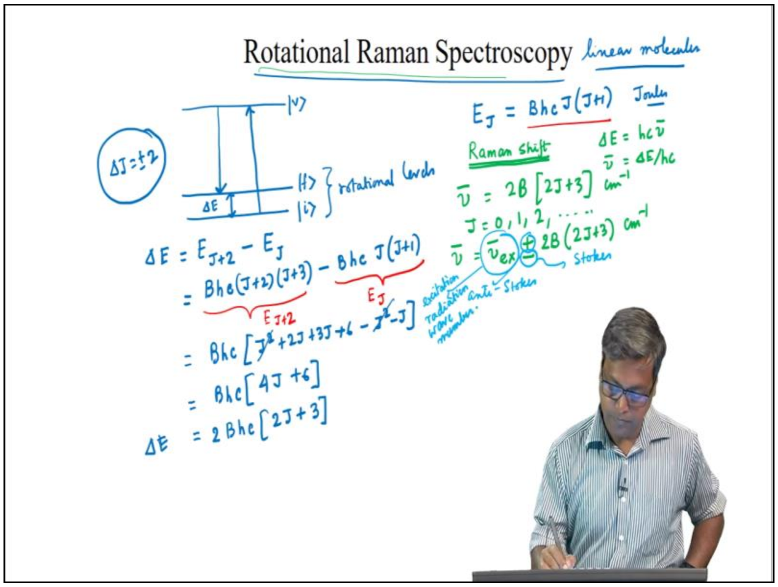

Rotational Raman Spectroscopy linear molecules

$E_J = BhcJ(J+1)$ Joules

$\Delta E = hc\bar{\nu}$

$\bar{\nu} = \Delta E/hc$

Raman shift

$\bar{\nu} = 2B[2J+3]$ cm^{-1}

$J = 0, 1, 2, \ldots$

$\bar{\nu} = \bar{\nu}_{ex} \pm 2B(2J+3)$ cm^{-1}

excitation radiation wave number.

Stokes

anti-Stokes

$$\Delta E = E_{J+2} - E_J$$
$$= \underbrace{Bhc(J+2)(J+3)}_{E_{J+2}} - \underbrace{BhcJ(J+1)}_{E_J}$$
$$= Bhc[\cancel{J^2} + 2J + 3J + 6 - \cancel{J^2} - J]$$
$$= Bhc[4J + 6]$$
$$\Delta E = 2Bhc[2J+3]$$

Hello all welcome to the lecture. In the last lecture we discussed about the quantum theory of Raman effect and we saw that the Raman transition happens through a virtual state. So, if we draw again the Raman process we will see that we have an initial state and a final state but the transition first happens from the initial state to a virtual state and from the virtual state it comes back to the final state.

Now if we compare this with a normal absorption process then the transition happens from the initial to the final state. So, as the transition probabilities are different for an absorption process and a Raman process we saw in the last lecture that the selection rule for the rotational Raman spectroscopy is also different. So, for rotational Raman spectroscopy the selection rule is Delta J equals +-2 and this is in contrast with the corresponding selection rule for the microwave spectroscopy where we have Delta J equals + or - 1.

So in rotational Raman spectroscopy we will first focus on linear molecules. So, let us draw again the Raman process we have the virtual state and the two other states here i and f are the rotational levels as we know for the rigid rotor model the energy of a molecule is given by E J where J is the rotational quantum number E J equals B hc J times J + 1 and the energy unit here is in Joule. Now the transition happens due to the selection rules and the selection rule is Delta J equals +- 2.

So during the transition so let us draw the transition here from the initial state it goes to the virtual state and from the virtual state it comes back to the final state. So, the change in energy due to the transition here is the energy difference between the initial and the final state that is Delta E and because the selection rule is Delta J equals +-2 we can write Delta E equals energy of J + 2 level - energy of the Jth level.

So this equals B hc times J + 2 times J + 3 - B hc times J times J + 1, so this first term is the energy of the J + 2 level where we have put J + 2 instead of J in this expression. And as we can see the second term is the energy of the Jth level. So, if we take B hc common what we get is J squared + 2 J + 3 J + 6 - J squared - J so J square J square cancels so what we get is B hc 4 J + 6. Now if we take 2 common what we get is 2B hc 2J + 3 so this is the energy difference or Delta E.

Now if we convert this energy difference into wave numbers which we will see is known as the Raman shift that is the shift from the excitation wavelength or wave number. And because we know Delta E equals hc nu bar we can write nu bar equals Delta E by hc. So, here we can write nu bar equals to be times 2J + 3 wave numbers. So, here J can take values from 0 1 2 dot dot dot. Thus if the molecule gains rotational energy from the photon during the collision we will have a series of lines to the lower wave number side of the excitation line.

This is because the molecule gains the energy. So, the scattered light loses energy and thus the lines appear at lower wave numbers and these lines are the Stokes lines. While if the molecule loses rotational energy to the photo on during collision we will have a series of lines to the higher wave number side of the excitation line. And these are the anti Stokes lines. The wave numbers of the corresponding spectral lines that we can observe in a rotational Raman spectrum are given by nu bar equals nu bar excitation + - 2B times 2J + 3 wave numbers.

So the plus sign here refers to the anti Stokes lines and the minus sign that means it goes to the lower wave numbers so, this minus sign refers to the Stokes lines. And this new E X is the wave number of the excitation radiation. So, this is the excitation radiation wave number.

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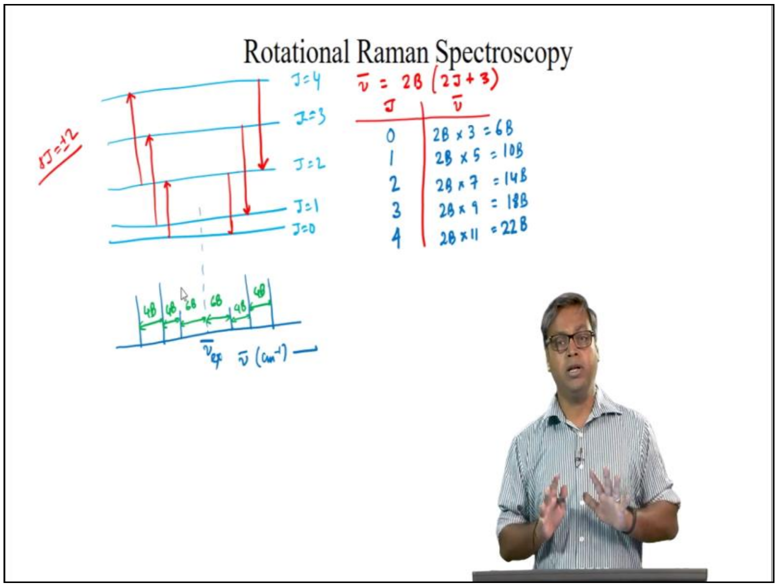

Rotational Raman Spectroscopy

$\bar{\nu} = 2B(2J+3)$

J	$\bar{\nu}$
0	$2B \times 3 = 6B$
1	$2B \times 5 = 10B$
2	$2B \times 7 = 14B$
3	$2B \times 9 = 18B$
4	$2B \times 11 = 22B$

So, let us now try to draw the allowed transitions. So, we have the rotational levels let us say we have J equals 0, J equals 1, J equals 2, J equals 3, and J equals 4. So, now if we draw the transitions we can draw because of the selection rule that is Delta J equals + - 2 from J equals 0 it will go to J equals 2 from J equals 1 it will go to J equals 3 and from J equals 2 it will go to J equals 4 and the reverse process is possible that means it will come from J equals to 2, J equals 0 J equals 3 to J equals 1 and from J equals 4 to J equals 2.

And we know that the shift the Raman shift is given by nu bar equals to B times 2J + 3 wave numbers. So, now if we draw a table so that we put the different values of J in the expression of nu bar the Raman shifts comes out to be so we have J here and nu bar here and let us say we put J equals 0, 1, 2, 3, 4. So, now for J equals 0 J bar is 2B times 3 that is 6 B for J equals 1 this is 2 B times 5 that is 10B and we have 2B times 7 that is 14B then we have 2B times 9 that is 18B and for J equals 4 it is 2B times 11 that is 22B.

So, let us now see how a rotational Raman spectrum would look like. So, here we have wave numbers that is nu bar in centimeter inverse and let us say this is my new bar excitation. So, we will have lines the anti-stokes lines will be like this and the Stoke lines will be like this. And now if you look into the table we will see the first line is shifted by 6B from nu bar excitation. So, the first line both on the left and on the right and all the other lines are shifted by 4B wave numbers.

So, this figure shows that typical rotational Raman spectra and as I have already mentioned the difference of the first line on either side from the excitation line is 6B while the separation between the successive lines are 4B. The relative intensities of the lines are indicated as you can see the way I have drawn the intensities are not the same. So, the relative intensities are indicated assuming the populations of the various rotational levels.

In particular it should be noted that the Stokes and the anti Stokes lines have comparable intensity because many rotational levels are populated. And hence the downward transition that is for the anti strokes lines are approximately as likely as the upward ones. And this is different from what we discussed in the last lecture for vibrational Raman where the anti Stokes lines were much weaker than the Stokes lines.

So, for diatomic and light triatomic molecules the rotational Raman spectrum will normally be resolved.

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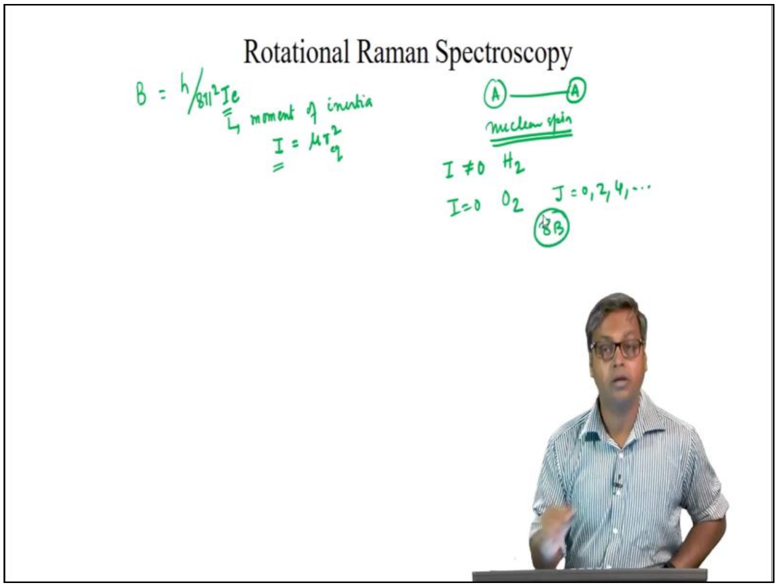

Rotational Raman Spectroscopy

$B = h/8\pi^2 I c$

moment of inertia

$I = \mu r_{eq}^2$

$I \neq 0$ H_2

$I = 0$ O_2 $J = 0, 2, 4, \ldots$

$\boxed{8B}$

The rotational Raman spectrum of a linear or diatomic molecule consists of a series of lines with constant gap for the centimeter inverse on either side of the excitation wavelength or wave number of the radiation. And if we recall the rotational constant B is given by h by 8 pi squared I c, where I is the moment of inertia and we know I equals mu r squared or r equilibrium squared where mu is the reduced mass and r equilibrium is the equilibrium bond length.

Thus determination of B enables the determination of the moment of inertia which further enables the bond length to be determined. It may be mentioned that homonuclear diatomic molecules are microwave inactive as they have no permanent dipole moment and as such the bond length of these homonuclear diatomic molecules cannot be determined using rotational or microwave spectroscopy. But rotational Raman spectra can be obtained for these diatomic homonuclear molecules.

Thus rotational Raman spectroscopy provides a method for the determination of the bond length in these molecules. But a note of caution is that for centrosymmetric molecules for example if you have a molecule which is A2 so it is a diatomic homonuclear molecule that is centrosymmetric. The effect of nuclear spin, so the effect of nuclear spin will be observed thus for hydrogen or other molecules for which the nuclear spin that is I is not equal to 0 the spectral lines show an alternation of intensity.

On the other hand for the case where I equal 0 for example I have oxygen for I not equal to 0 the example was hydrogen. So, for I equal to 0 the energy levels with even values of J that is J equals 0 to 4 etcetera will be missing thus the alternate lines will be missing and the gap between the successive lines instead of 4B will now be 8B. So, we will discuss this in the next lecture and we will end today's lecture by solving a couple of problems.

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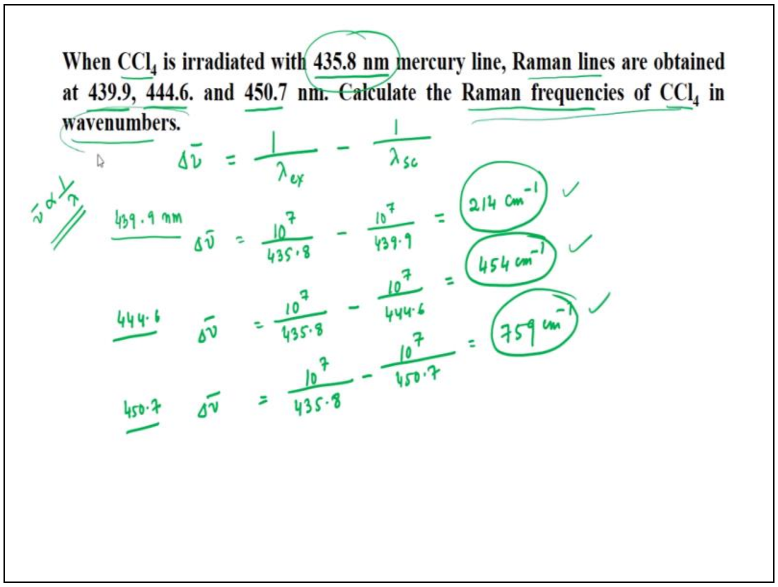

When CCl_4 is irradiated with 435.8 nm mercury line, Raman lines are obtained at 439.9, 444.6. and 450.7 nm. Calculate the Raman frequencies of CCl_4 in wavenumbers.

$$\Delta\bar{\nu} = \frac{1}{\lambda_{ex}} - \frac{1}{\lambda_{sc}}$$

$\bar{\nu} \propto 1/\lambda$

439.9 nm $\quad \Delta\bar{\nu} = \frac{10^7}{435.8} - \frac{10^7}{439.9} = \boxed{214\ cm^{-1}}$ ✓

444.6 $\quad \Delta\bar{\nu} = \frac{10^7}{435.8} - \frac{10^7}{444.6} = \boxed{454\ cm^{-1}}$ ✓

450.7 $\quad \Delta\bar{\nu} = \frac{10^7}{435.8} - \frac{10^7}{450.7} = \boxed{759\ cm^{-1}}$ ✓

So, we have the first problem here when carbon tetrachloride or CCl4 is irradiated with 435.8 nanometer multiline Raman lines are obtained at 439.9, 444.6 and 450.7 nanometer. So, we have to calculate the Raman frequencies of CCl4 in wave numbers. So, we know that the shift that is delta nu bar between the successive lines or between the X addition line and any Raman line is given by 1 by lambda excitation - 1 by lambda scatter.

And this is because we know that nu bar is inversely proportional to lambda. So, now let us look for the first line here the first line comes up, 439.99 nanometer. So the delta nu bar will be 10 to the power 7 by 435.8 because this is the excitation wavelength - 10 to the power 7 divided by 439.9 and this is equal to 214 centimeter inverse. So, this is the Raman frequency of the first line of CCl4 in wave numbers. Now if we look into the second line that is 444.6 Delta nu bar equals 10 to the power 7 by 435.8 - 10 to the power 7 divided by 444.6 so that is 454 centimeter inverse.

And for the third line in nanometer is 450.7 so Delta Nu bar we can write 10 to the power 7 divided by 435.8 - 10 to the power 7 divided by 450.7 and that is 759 wave numbers. So, these are the 3 Raman frequencies of CCl4 in wave numbers.

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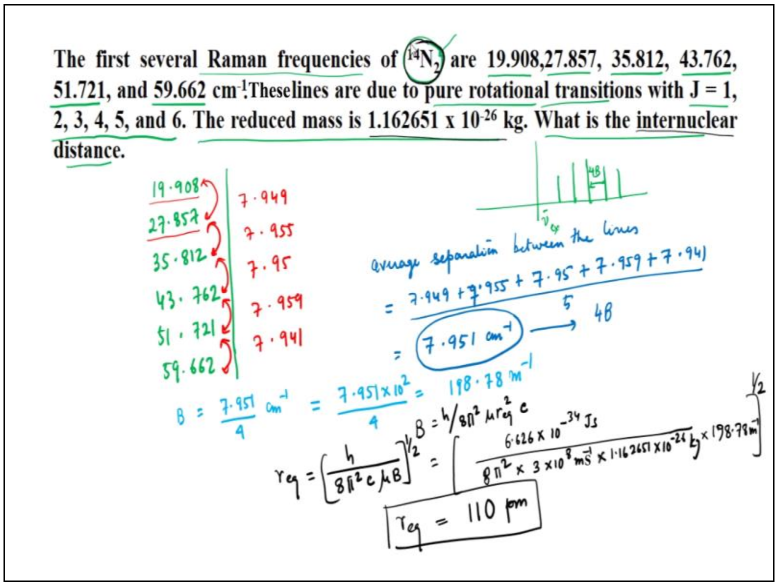

The first several Raman frequencies of $^{14}N_2$ are 19.908,27.857, 35.812, 43.762, 51.721, and 59.662 cm^{-1}.Theselines are due to pure rotational transitions with J = 1, 2, 3, 4, 5, and 6. The reduced mass is 1.162651×10^{-26} kg. What is the internuclear distance.

19.908	
27.857	7.949
35.812	7.955
43.762	7.95
51.721	7.959
59.662	7.941

average separation between the lines

$$= \frac{7.949 + 7.955 + 7.95 + 7.959 + 7.941}{5}$$

$$= \boxed{7.951\ cm^{-1}} \longrightarrow 4B$$

$$B = \frac{7.951}{4}\ cm^{-1} = \frac{7.951 \times 10^2}{4} = 198.78\ m^{-1}$$

$$B = h/8\pi^2 \mu r_{eq}^2 c$$

$$r_{eq} = \left[\frac{h}{8\pi^2 c \mu B}\right]^{1/2} = \left[\frac{6.626 \times 10^{-34}\ Js}{8\pi^2 \times 3 \times 10^8\ ms^{-1} \times 1.162651 \times 10^{-26}\ kg \times 198.78\ m^{-1}}\right]^{1/2}$$

$$\boxed{r_{eq} = 110\ pm}$$

So, now let us look into the next problem the first several Raman frequencies of nitrogen 14 are 19.908, 27.857, 35.812, 43.762, 51.721 and 59.662 wave numbers. So, these lines are due to pure rotational transitions with J equals 1 2 3 4 5 and 6. The reduced mass of nitrogen14 is given. So, the question is what is the internuclear distance. So, again see this is a homonuclear diatomic molecule and Raman spectrum could be taken and all we need to do now is to find the internuclear distance of this homonuclear diatomic molecule.

So let us first make a table of the different transitions first is 19.908, 27.857, 35.812, 43.762, 51.721 and 59.662. So, we know that if we draw a rotational Raman spectrum and let us say this is the nu bar excitation all these different lines are separated by 4B. So, let us try to find the separation here. The separation for the first case if we do let us say 27.857 - 19.908 the separation will be 7.949 wave numbers.

So now if I take the separation between the second and third is 7.955 for the third and fourth it is 7.95 between the fourth and fifth it is 7.959 and between the fifth and sixth it is 7.941. So, you see these numbers are slightly different so what we will take the average separation. So, now if you take the average separation for this we need to add this up that is 7.949 + 7.955 + 7.95 + 7.959 + 7.941 and we have two divided by the number of points we have that means 5.

So, this answer will be 7.951 centimeter inverse and this is the average separation between the lines. So, this 7.951 is actually 4B. And now this means B equals 7.951 divided by 4 wave numbers or centimeter inverse. So, we can write this as 7.951 times 10 to the power 2 divided by 4 that is 198.78 meter inverse. So, we know that B is given by h by 8 pi squared and if we expand the moment of inertia we get mu r equilibrium square times C.

So we can write r equilibrium equals h by 8 pi squared C mu B to the power half. So, we will put the values here now that h is 6.626 times 10 to the power -34 Joule-seconds. Then we have 8 pi squared then we have speed of light that is 3 times 10 to the power 8 meter seconds inverse and then we have the reduced mass which is given here. So, this is 1.162651 times 10 to the power -26 kg and we have B which is given by 198.78 meter inverse.

So we have whole to the power half and if we do this math the internuclear distance that is our quilibrium what we get is 110 Pico meter. So, this is the answer we needed to calculate that is the internuclear distance between the 2 nitrogen atoms of n14.