This topic is from the program TYBSc

subject chemistry semester 5 code

of the courses CHC-105 and title of

the course Physical Chemistry.

The title of the unit is Molecular

Spectroscopy-2 and name of the module

is computation of force constant.

The outline of this presentation will

include understanding about force

constant and we are going to solve

some problems based on force constant.

Students will understand what is

force constant and its relation

with the vibrational frequency

and numerical on force constant.

So when we have a diatomic molecule,

diatomic in the sense

consisting of two atoms,

let's say the mass of 1 atom is m_1

and the mass of another atom is m_2.

Now when we have a diatomic molecule,

they are bonded by a chemical bond.

And this bond has an ability to vibrate,

so when a direct diatomic molecule with

atomic masses m_1 and m_2 are joined by a

chemical bond and it vibrates as a one

dimensional simple harmonic oscillator,

classically the vibrational frequency v

of a mass point which is connected by a

force constant K is given by mv is equal to.

$1/2\pi * (k/m)^{1/2}$.

If you see the figure there are two

atoms of masses m_1 and m_2 shown in

greenish color which is having a bond

between them shown in the blue color.

So in such a system.

The masess m_1 and m_2.

They can vibrate back and forth.

Which is relative to the centre of

the mass in opposite directions.

So when we have two masses which

reach extreme of their

respective motions at the same time,

the vibrational frequency of the

molecule is given by the relation

analogous to that of the equation 1.

With the mass M replaced by the reduced mass.

So if you see the first

equation here in place of m,

we are substituting μ

What is the difference?

It is m is the mass and μ is

the reduced mass.

So next is this unit of

frequency is taken inverse.

So if we want to convert the unit

of the frequency from second

inverse to centimeter inverse,

we have to divide it by see

that is the velocity of light.

So that is how the term c which comes

into picture in your equation #3.

So we write in place of v.

We write $\bar{\nu}$ which is equal to

$$\frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

In centimeter inverse,

so we are going to use the equation 3

while solving the problem that

is $\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$ cm^{-1}

So the first problem.

The fundamental vibrational frequency

of is given as 2890 centimeter inverse.

We are asked to calculate the

force constant of this molecule.

Now when we have HCl, the atomic

masses of H and Cl is also given,

so the atomic masses of H is given as

$1.673 \times 10^{(-27)}$.

And Cl is $58.06 \times 10^{(-27)}$ kg.

Now you see if you see the problem we

are given the vibrational frequency.

We are asked to calculate the force

constant and we are given atomic masses.

So as I said we have to use the formula.

$$\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

So if we consider this particular

formula you see $\bar{\nu}$ is given

as 2890 cm^{-1}.

We know the value for velocity of light,

it is $3 \times 10^{(10)}$ cm,

while we

are taking in centimeter because all

the units should be in centimeter.

Then we have to calculate μ.

μ is equal to how to calculate

μ when we replaced mass with μ,

we should also know how to calculate

μ using m.

So the formula to calculate μ

is m_1 m_2 divided by m_1+m_2.

So when we have a diatomic

molecule which is containing of

hydrogen and chlorine atom,

we can take m_1 as a mass of

hydrogen and m_2 as a mass of

chlorine and we can just substitute.

Hitting the formula of v is equal

to m_1 into m_2 divided by m_1 plus m_2.

So we just did that m_1 $1.673 \times 10^{(-27)}$,

and m_2 $58.06 \times 10^{(-27)}$.

We have substituted in the formula

and we get $1.626 \times 10^{(-27)}$ kg so we

have calculated the reduced mass

using the masses of two atoms.

So now if you see the formula there.

$\bar{\nu}$ is equal to $\frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$

So from that formula we have $\bar{\nu}$,

we know what is $\bar{\nu}$, we know what is c.

We also know what is π.

And we also calculated μ.

So what is left is K,

that is the force constant.

So let's rewrite and rearrange the

formula in such a way that we keep

the unknown to one side and all

other terms to the right hand side.

So when we work it out K.

Become equal to

$4\pi^2 c^2 (\bar{\nu})^2$ μ

so this is after rearrangement

of the main equation.

Now we just have to substitute

the value for π, then four,

then $\bar{\nu}$ and μ.

Once we substituted all these values,

we get $4.83 \times 10^{(2)}$ kg m s^{-2} m^{-1}

Now we just have to convert this to

Newton per metre because force constant

is always expressed in Newton per meter.

Now how to convert kilograms

Seconds square per meter inverse?

This is by dividing the value by 100,

so we get 4.83 Newton per meter.

So this is how if we are given

vibrational frequency of a molecule

we can calculate the force constant.

If we know the masses of the

atoms in a diatomic molecule.

Now this is the second numerical

based on force constant.

Now we have carbon monoxide molecule.

So in this problem what is given is the

force constant of carbon monoxide is

given which is 1840 Newton per meter.

We have to calculate the vibrational

frequency in centimetre inverse and

the spacing between the vibrational

energy levels in electron Volt.

So compare this spacing with the

thermal energy at room temperature

and comment on your result.

Now the atomic masses are also given.

It is for carbon,

it is $19.9 \times 10^{(-27)}$ and for oxygen.

It is $26.6 \times 10^{(-27)}$

Now that we are asked to find the

value in terms of electron Volt,

the conversion factor is also given.

One electron Volt is 8066 centimeter inverse,

so we have to use the same formula

because all the values are

given in terms of centimeter inverse.

$$\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

Now the force constant is given k is given,

we can calculate μ using the

mass of carbon and oxygen.

So similarly,

the way we have done for the earlier problem.

So μ is equal to $m_1 m_2$

divided by m_1 plus m_2.

So let's consider m_1 is the mass of

carbon and m_2 is a mass of oxygen.

So our m_1 will be $19.9 \times 10^{(-27)}$ kg

And m_2 will be $26.6 \times 10^{(-27)}$ kg.

Just substituting it in the formula,

we get $11.4 \times 10^{(-27)}$ as a reduced mass.

So if you see the formula we have,

we know the value of Pi.

We know the value of c.

We know the value of k which is given

and we calculated the value of $\bar{\nu}$.

So if we just substitute all these values.

That is k μ and c and pi we get.

2140 centimeter inverse as the

vibrational frequency of a molecule.

Next we have to calculate the

spacing between the vibrational

energy levels and this spacing.

We have to convert in terms of electron Volt.

So we know that from the vibrational Spectra

that Delta E is equal to $E_{(v+1)} - E_v$.

What is the meaning?

This is if we consider Delta E.

Consider the difference between

the level that is E_2 & E_1.

Let's say if V is equal to 1 and

we substitute one in place of

v then it is $E_2 – E_1$, if V is

equal to two then it will be $E_3 - E_2$.

So, delta E is always equal to

$E_{(v+1)} - E_v$ incase of vibrational Spectra

and Delta E is equal to hv.

Now if we want to convert it

from joules to centimeter inverse,

we divide it by hc so we get $\bar{\nu}$.

So delta is equal to $\bar{\nu}/c$.

So again we have to.

We cannot take the value in terms

of centimeter inverse because we

have to convert it in terms of.

eV so we can directly convert

it and take delta E is equal to 2140

centimeter inverse divided by 8066

centimeter inverse upon electron Volt.

So once we do that you see centimeter

inverse and centimeter inverse

will get cancel out and electron

Volt will come in the numerator.

So Delta E will be equal to

0.265 electron Volt.

So this is what is the

second part of the problem.

That is, we are asked to calculate

the spacing between the vibrational

energy levels in eV

Next is we have to compare this spacing

whatever value we have obtained.

We have to compare this spacing with

the thermal energy at room temperature

and once we compare it with the

thermal energy at room temperature,

we have to comment on the result.

So let's first see what we get.

The value for thermal energy.

So thermal energy is given in terms of kT.

So once we substitute these values in terms

of kT and divide it per electron Volt.

We get 0.026 electron Volt.

Now we see thermal energy value

is 0.026 electron Volt and delta

E is 0.265 eV.

So the one which is higher is delta E.

So thermal energy is less than Delta E.

kT is less than delta so when

such a condition is there we can

conclude that most of the molecules

are in the ground vibrational state.

At room temperature.

And this situation is in contrast with

the rotational states in rotational states,

kT is higher than delta.

That means most of the molecules

are in the excited rotational

state at room temperature.

This is a reference.

Thank you.