Fundamentals of Spectroscopy

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Lecture – 10
Different Forms of Spectroscopy

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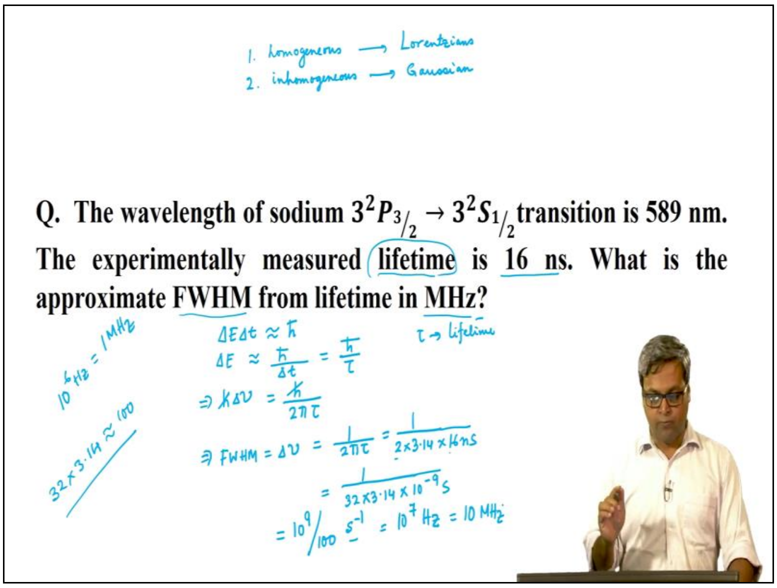

1. homogeneous → Lorentzians
2. inhomogeneous → Gaussian

Q. The wavelength of sodium $3^2P_{3/2} \rightarrow 3^2S_{1/2}$ transition is 589 nm. The experimentally measured lifetime is 16 ns. What is the approximate FWHM from lifetime in MHz?

$\tau \rightarrow$ lifetime

10^6 Hz = 1 MHz

$32 \times 3.14 \approx 100$

$$\Delta E \Delta t \approx \hbar$$
$$\Delta E \approx \frac{\hbar}{\Delta t} = \frac{\hbar}{\tau}$$
$$\Rightarrow \cancel{h}\Delta\nu = \frac{\cancel{h}}{2\pi\tau}$$
$$\Rightarrow \text{FWHM} = \Delta\nu = \frac{1}{2\pi\tau} = \frac{1}{2\times 3.14\times 16\,\text{ns}}$$
$$= \frac{1}{32\times 3.14\times 10^{-9}\,\text{s}}$$
$$= 10^9/100\ \text{s}^{-1} = 10^7\ \text{Hz} = 10\ \text{MHz}$$

In the last lecture we discussed line shape functions we saw there are two categories of line broadening one is homogenous and the other one is inhomogeneous. So, homogeneously broaden lines we saw are represented by Lorentzian line shape functions on the other hand the inhomogeneously broaden lines are represented by Gaussian line shape functions. So, before we start a new topic in today's lecture let us first look into a problem that involves line shape function.

So, we have a question here the wavelength of a certain transition of sodium is 589 nanometer the experimentally measured lifetime is 16 nano second so the question is what is the approximate full width half maximum from lifetime and you have to find the F W H M in megahertz, so this is the question. So, yesterday we saw from Heisenberg's uncertainty principle we can write Delta E times delta T is approximately h cross.

So now delta T we can think is the time that the molecule survives in the excited state or that is the life time. So, we can write Delta E approximately equals h cross by delta T or h cross by tau where tau is the life time. So, delta E we can write h delta nu and that is equals h by 2 pi tau so we cancel h h then the full width at half maximum is given by delta nu that is equal to 1 by 2 pi tau. So, now we will put the values 1 by 2 times 3.14 times 16 nano second.

So, we can write that as 1 by 2 times 16 is 32 times 3.14 times 10 to the power -9 seconds. So, this is 10 to the power 9 by 100 because 32 times 3.14 is approximately 100, so 10 to the power 9 by 100 second inverse so second inverse is Hertz so that is 10 to the power 7 Hertz. But we have to find the answer in mega Hertz so we know that 10 to the power 6 Hertz equals 1 mega Hertz so 10 to the power 7 Hertz is 10 mega Hertz. So, the answer is the full width at half maximum is 10 megahertz.

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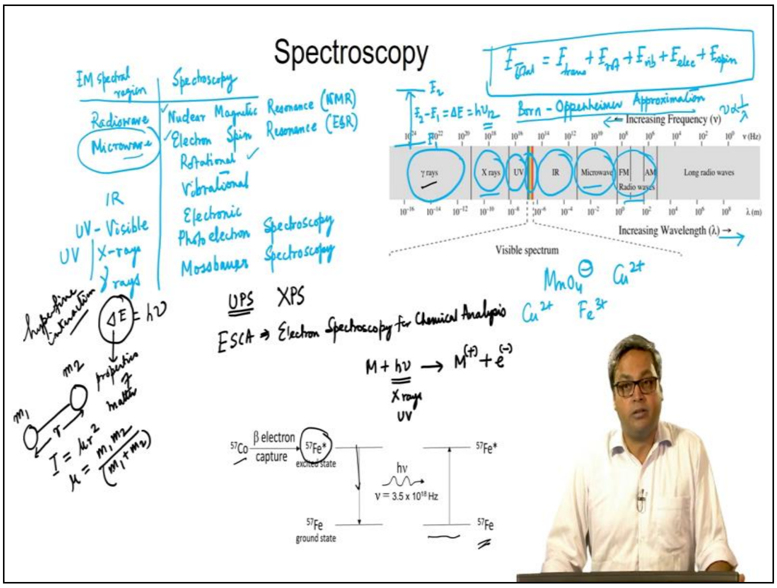

Spectroscopy

$E_{Total} = E_{trans} + E_{rot} + E_{vib} + E_{elec} + E_{spin}$

Born - Oppenheimer Approximation

$E_2 - E_1 = \Delta E = h\nu_{12}$

$\nu \propto \frac{1}{\lambda}$

EM spectral region	Spectroscopy
Radiowave	Nuclear Magnetic Resonance (NMR)
Microwave	Electron Spin Resonance (ESR)
	Rotational
IR	Vibrational
UV - Visible	Electronic Spectroscopy
UV | X-rays	Photoelectron Spectroscopy
γ rays	Mossbauer Spectroscopy

UPS XPS

ESCA → Electron Spectroscopy for Chemical Analysis

$M + h\nu \rightarrow M^{(+)} + e^{(-)}$

X rays

UV

$MnO_4^{\ominus}$ Cu^{2+} Cu^{2+} Fe^{3+}

$\Delta E = h\nu$

properties of matter

hyperfine interaction

$I = \mu r^2$

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

In the last few lectures we had a general description of light matter interaction and discussed about the various concepts which are generally common in any kind of spectroscopy. By now we know that depending on the frequency of light or the wavelength of light we can have different forms of spectroscopy today we will have a general discussion about this difference spectroscopy. So, we know that different modes of motion are possible for a molecule.

So the total energy are E total the total energy can be grossly written as a sum of energies of different degrees of freedom for example I can write E total equals E translational + E rotational + E vibrational + E electronic + E spin. So, we can write the total energy as a sum of this different energies. So, when we discussed about any spectroscopic transitions happening between two levels E 1 and E 2. So, we saw that E 2 - E 1 that is Delta E is given by h nu 12 where nu 12 is the frequency of light.

So, these gaps between the energy levels that is Delta E are widely different for different degrees of freedom thus when one motion is excited the energy of the other modes can be assumed to remain unchanged. So, this is an approximation known as Born Oppenheimer approximation. So, we will discuss this Born-Oppenheimer approximation later in a greater detail. So, when Delta E for a particular degree of freedom matches the frequency of the electromagnetic radiation we have a certain form of spectroscopy.

For example Delta E value for vibrational motion that is difference in energy between the different vibrational levels when these Delta E matches the h nu value in the infrared or the IR region of the electromagnetic radiation we have IR spectroscopy which is also known as vibrational spectroscopy. So, let us look into the electromagnetic spectrum. So, as we see the entire electromagnetic spectrum can be divided into different regions but before we look into the different regions we should see that in this figure the wavelength is increasing to the right and frequency which is inversely proportional to wavelength is therefore increasing to the left.

So, we see that we have different regions we have radio waves then we have microwave if we actually go for more larger frequency we have IR then we have visible then ultraviolet or UV then x-rays and finally the gamma rays. So, in general we have different spectroscopy for different regions of the electromagnetic spectrum. So, let us try to make a table so we will have two columns in one column we will put the electromagnetic spectral region.

And in the other column we will put the spectroscopy associated with this particular region. So, let us start with radio waves so in the radio wave range we have something known as nuclear magnetic resonance spectroscopy or in short known as NMR. So, then we have the microwaves so in the microwave we have electron spin resonance or in short known as ESR in the microwave region. We can also have rotational spectroscopy then we have the infrared or the IR so we have vibrational spectroscopy in this region.

And then we have visible so we will club together the ultraviolet and visible and here we have electronic spectroscopy. So, then we have after ultraviolet we have x-rays so x-rays we have photo electron spectroscopy. So, we can also have photoelectron spectroscopy if we use high energy UV light. And finally gamma rays for gamma rays we have mossbauer spectroscopy. So, let us first start with NMR and ESR so these are examples of resonance spectroscopy.

In fact the R in NMR and the ESR stands for resonance due to the existence of spin it can be a nuclear spin or an electronic spin. So, a nucleus or an electron has a magnetic moment in the presence of an external magnetic field the vector representing the magnetic moment undergoes a processional motion around the external magnetic field. And the frequency of this processional motion is a property of the matter or the spin system.

So when this frequency matches with the frequency of the electromagnetic wave falling on the system and absorption of radiation takes place. This is the origin of NMR or ESR since spectroscopic transition takes place under the condition of equality of the two frequencies one of light that is the electromagnetic wave and the other of matter that is due to the spin system. So, this form of spectroscopy happening under the condition of equality of the two frequencies is called resonance spectroscopy.

However depending on the delta E value the nuclear spin system absorbs in the radio frequency region hence the name nuclear magnetic resonance or in short NMR is given. Similarly Delta E for electron spin system matches with the energy of the microwave region hence ESR takes place in the microwave region of the electromagnetic spectrum. So, in this table after yes our we have rotational spectroscopy we do not talk about translational spectroscopy this is because the gap between the translational energy levels is very, very small.

Compared to the thermal energy or KT and thus translational energy of a molecule can be considered as almost continuous hence translational spectroscopy is not possible. The other modes of nuclear motion in a molecule are rotation and vibration note that the rotation and vibration is not possible for atoms so thus only for molecules we have quantized rotational and quantized vibrational levels. The energy gap between the rotation and levels is of the order of the energy in the microwave region.

Hence in the microwave region we also have rotational spectroscopy or microwave spectroscopy which involves transitions between quantized rotational levels. Similarly we have vibrational or IR spectroscopy in the infrared region which involves transitions between quantized vibrational levels. So, spectroscopy involving transition between the electronic levels appear in the ultraviolet or visible region.

Thus in the ultraviolet or visible region we have electronic spectroscopy due to transition in the visible region the matter or the molecule absorbs a portion of the light from the visible region this is the origin of colour of a compound. Thus if we have like Mno 4 minus or Cu 2 plus so these ions absorb energy in the visible region or we can say the undergo transitions between the electronic energy levels and appear to be coloured.

On the other hand ethylene or acetone so these molecules undergo electronic transition but the Delta E value corresponds to the ultraviolet region and not the visible region. And thus they appear to be colourless. So, note that molecular spectroscopy involves rotational vibrational and electronic spectroscopy. But for atoms or let us say free ions for example Cu 2 + or Fe 3 + for these ions and atoms we only have electronic transitions. If one uses photons of higher frequency that is of higher energy then effects other than spectroscopic transitions may take place.

Thus if one shines x-ray or high-energy ultraviolet light on matter the bound electrons in the atoms or molecules may be knocked out and photo electrons are formed. So, we can write M that is matter plus h nu there is an energy from the x-rays or high energy UV light such that M becomes ionized that is M+ and the electron is knocked off that is plus electron. The ejected electrons have different kinetic energy values depending on how strongly bound the electron was in the atom or molecule.

Thus one can study the kinetic energy of ejected electrons and get an energy spectrum this is commonly known as photoelectron spectroscopy and provides information about the binding energy or the ionization energy of an electron in a molecule. Intuitively an electron which is far away from the nucleus that is the outer electrons involved in bonding have lower energy and thus they can be ejected if one uses ultraviolet light.

Thus ultraviolet photoelectron spectroscopy also known as UPS that is ultraviolet photoelectron spectroscopy provides information about the valence electrons that is for example the 2S or the 2P electrons in carbon on the other hand high-energy radiation like x-ray can knock out the electrons close to the nucleus that is the core electron. For example the 1s electrons of carbon and hence information about the binding energy of the core electrons can be obtained from x-ray photoelectron spectroscopy or which is also known as XPS.

It may be pointed out that when bonding between atoms take place to form molecules this involves the valence electrons only the core electrons are not involved and their binding energy with the nucleus is least affected. Thus one expects that XPS faithfully reports the signature of atoms in molecules. As a result chemical elemental analysis can be done using XPS. This procedure is known as ESCA or electron spectroscopy for chemical analysis.

Gamma-ray spectroscopy involves emission and subsequent absorption of a gamma-ray photon this spectroscopy is named as Mossbauer spectroscopy a heavy nucleus when formed by the radioactive decay of an isotope is often produced in the excited state. So, let us take the following example; so 57 cobalt by an electron capture produces 57 iron in the excited state which rapidly drops to the ground state 57 iron by emitting a gamma-ray photon.

If a second nucleus initially in the ground state is put in the emitted radiation it is expected to absorb the photon this is known as resonance absorption. But such a resonance absorption does not take place normally because of the recoil of the nucleus emitting the photon. So, Mossbauer or gamma ray spectroscopy is the study of absorption of the gamma ray photon under the condition of no recoil.

So, if we put the sample in a solid matrix instead of a solution then we can minimize this requirement so in this Picasa P a transition between the nuclear energy levels of the atom takes place these levels are slightly modified by the surrounding nuclei which is known as hyper fine interaction. And thus Mossbauer spectroscopy can give information about the electronic environment of the nucleus for this reason Mossbauer spectroscopy is important to a chemist who mainly deals with the electronic environment in molecules.

So, another type of spectroscopy is known this is Raman spectroscopy this spectroscopy differs from the other spectroscopy is discussed so far. In other spectroscopy that we have discussed a transition takes place from the initial stationary state to the final stationary state directly but in Raman spectroscopy our direct transition between the initial stationary state and the final stationary state does not happen.

So, rather transition takes place via an intermediate virtual state. So, later we will discuss most of these different forms of spectroscopy in greater detail. But a general question that comes up is what different information about the matter can we obtain from these different spectroscopy for this let us visit the Bohr condition which is given by delta E equals h nu as we have already discussed the left hand side of the Bohr condition that is Delta E provides us with the properties of matter.

So we can use different spectroscopy to study different properties of matter in other words we can get information of the motion corresponding to the energy level associated by the light matter interaction. So, for example we can get rotational characteristic from rotational spectroscopy. So, rotational spectroscopy involves moment of inertia which is given by I, I is given by mu r square for a diatomic molecule.

So, for a diatomic molecule with mass m1 of one atom and n2 for the other atom and let us say r is the bond length so mu is the reduced mass which is given by m1 m2 by m1 + m2 so we can get information about bond length of diatomic molecules for example HCl from rotational spectroscopy. We will discuss in details when we study rotational spectroscopy later. IR spectroscopy provides us information about vibrations.

So, when a bond vibrates the vibrational frequency depends on the bond strength or force constant of the bond. So, we can get information on bond strength of different bonds in a molecule from IR spectroscopy. Similarly NMR or ESR spectroscopy provides information about the molecular structure. So, we can see that different spectroscopy provide us different information about the molecule or about the matter.

So, we will discuss these again when we will learn the different forms of spectroscopy in greater details in the later lectures.