Nuclear probes: Positron annihilation spectroscopy

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Lecture-19, Module-1

Hello everyone. So, we have been discussing different techniques, particularly nuclear analytical techniques last few lectures like neutron activation analysis, ion beam analysis, wherein we utilize the nuclear phenomena to determine to determine the concentrations or even to get profile the elements in the matrix. As you recall, we call nuclear chemistry as a subject where we use chemical techniques like radio-chemical separations to understand the nuclear properties of elements, nuclear phenomena and radio chemistry as you know, we use radiations emitted by the elements to study their chemical properties. Today, I am going to discuss a topic of research, another frontier researcher, wherein we use nuclear phenomena in understanding problems in physics and chemistry and other areas. So, the nuclear chemistry has thrown some probes, which we will discuss in today's lecture. Those probes we can utilize in understanding processes and phenomena in sciences.

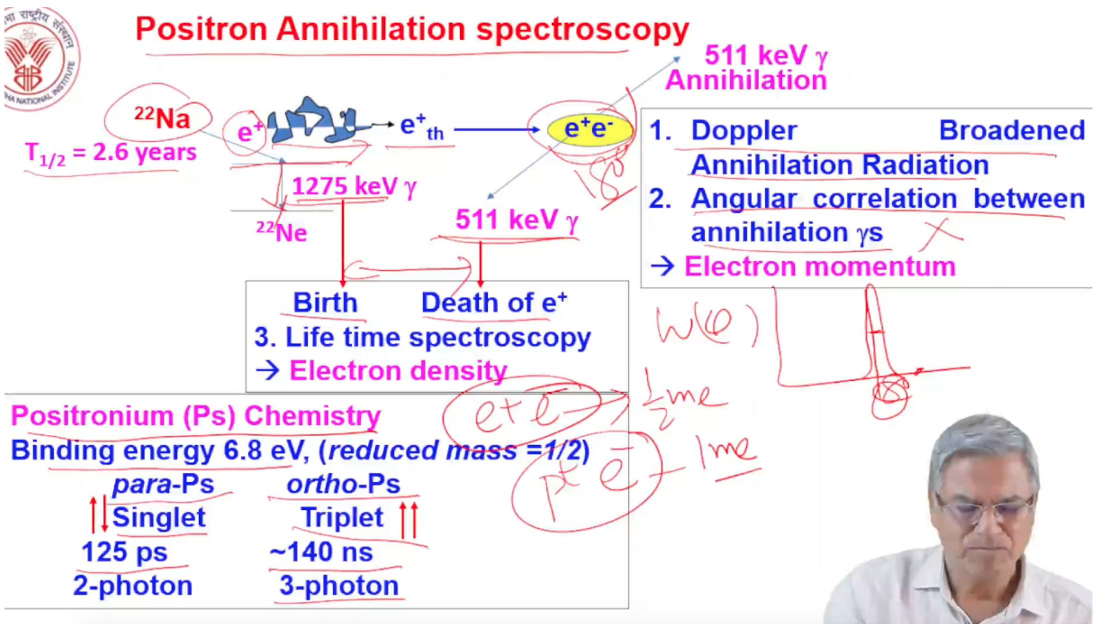
Nuclear Probes in chemistry

1. Positron Annihilation Spectroscopy (PAS)
2. Perturbed Angular Correlation (PAC)
3. Mossbauer Spectroscopy

So, we call them as nuclear probes. Let us see what are these nuclear probes and especially in chemistry. Of course, now we do not have well-defined boundaries. There is a lot of research in the multidisciplinary subjects.

We have chemical physics and physical chemistry and that at the boundary of physics and chemistry. So, when I say nuclear probes, it can be applied to physical chemistry, chemical physics and so on. So, there are three techniques which are coming in the category of nuclear probes. One of them is the positron annihilation spectroscopy. I will discuss it more in detail. Perturbed angular correlation spectroscopy (PAC) and the third is Mossbauer spectroscopy.

Some of you may be knowing about Mossbauer spectroscopy. Mossbauer spectroscopy relies upon the recoil less absorption. A low energy gamma is emitted by a nucleus in its excited state and the same gamma is absorbed by another nucleus in the sample. So, the source is emitting that low energy gamma and the sample is absorbing and to take care of the recoil and the Doppler broadening, the sample is kept in a crystalline state and also at low temperature and the source is moved towards the sample at different velocities to take care of the Doppler effect. So, all these things are coming in the category of Mossbauer spectroscopy and it is quite popular, but that has got a limitation on the number of nuclei that you can use like for example, ^{57}Fe, you can study the iron chemistry or tin chemistry, hafnium chemistry, certain nuclei are amenable to Mossbauer spectroscopy. So, I will not discuss this particular topic. I will discuss the positron annihilation spectroscopy and perturbed angular correlation spectroscopy.



Okay, so first let me discuss what is this positron annihilation spectroscopy. And I will give you an example of a source, radioactive source which emits positrons. You can use a positron source, positron emitter, of course it should have sufficiently long half-life so that you don't need to change the source repeatedly. And how this positron can be made use of in understanding chemical processes or physical processes. This let me try to explain using this slide. So, when this positron is emitted by the radioactive source, then this positron like if you recollect the interaction of fast electrons, electrons and positrons with matter, the energy of the positron will be few hundreds of keV. Now this positron will slowly interact with the electrons in the medium and it will slow down by elastic scattering and when it becomes thermalized, the positron which is thermalized undergoing a tortuous path, then this thermalized positron can undergo different types of interactions.

So one of them is annihilation with an electron, the positron is thermalized, it has no momentum and when it is annihilating with the electron, you get two photons of 511 keV each. The rest mass of electron positron pair is 1.02 MeV and so that leads to the gamma ray photons 1.02 MeV split into two photons of 511 keV each and because the initial momentum is zero, the two photons are emitted at 180 degree, then we call them as annihilation gamma rays. Now what happens that if the electron with which the positron is annihilating is not stationary, it has certain momentum, then the positron annihilating with an electron which is in motion and hence has some momentum, then 511 keV gamma line will get broadened. That means it will not be exactly 511, it will be 511 ± ΔE because of the momentum of the electron. And so there comes the technique called Doppler broadened annihilation radiation (DBAR). So this 511 keV gamma ray is broadened because of the Doppler broadening of because of electron momentum. And we can make use of that broadening to determine the electron momentum.

Secondly, these two 511 keV gammas are emitted at 180-degree angle because of the same process that is the conservation of linear momentum. And so the angular correlation between these two gamma rays, that means if you measure the coincidence counts as a function of θ, W(θ) versus θ, then we should get a line at 180 degrees. But because of the electron momentum, there is a angular correlation. So at some degrees plus and minus 180, there are some counts. So this angular correlation deviation from 180 degree is again because of the momentum of the electron. So you can study the electron momentum, what type of electrons are involved when the positron is annihilating.

So these are the two techniques, Doppler broadened annihilation radiation, and angular correlation between the electron. So we will not talk about this angular correlation, it can also be used to obtain the electron momentum.

And third technique is like when the ^{22}Na source decays by positron to this excited state of 22Ne, this is emitting a gamma ray of 1275 keV. So the lifetime of this intermediate level, excited level is very, very short, less than a picosecond. And so this 1275 keV gamma is emitted almost instantaneously following the decay of ^{22}Na. So we can say that this 1275 keV gamma ray tells you the time when the positron was born. And subsequently, the positron is thermalizing, interacting with the electron and annihilating with the electron to give you a 511 keV gamma ray. So that tells you the death of the positron. Positron is finished now. And the time difference between these two events is called the lifetime of positron. So depending upon the environment, chemical environment in which the positron is dying or positron is annihilating with an electron, this lifetime can change. And so this lifetime essentially tells you about the electron density in the medium where the positron is annihilated. So this is another experimental technique.

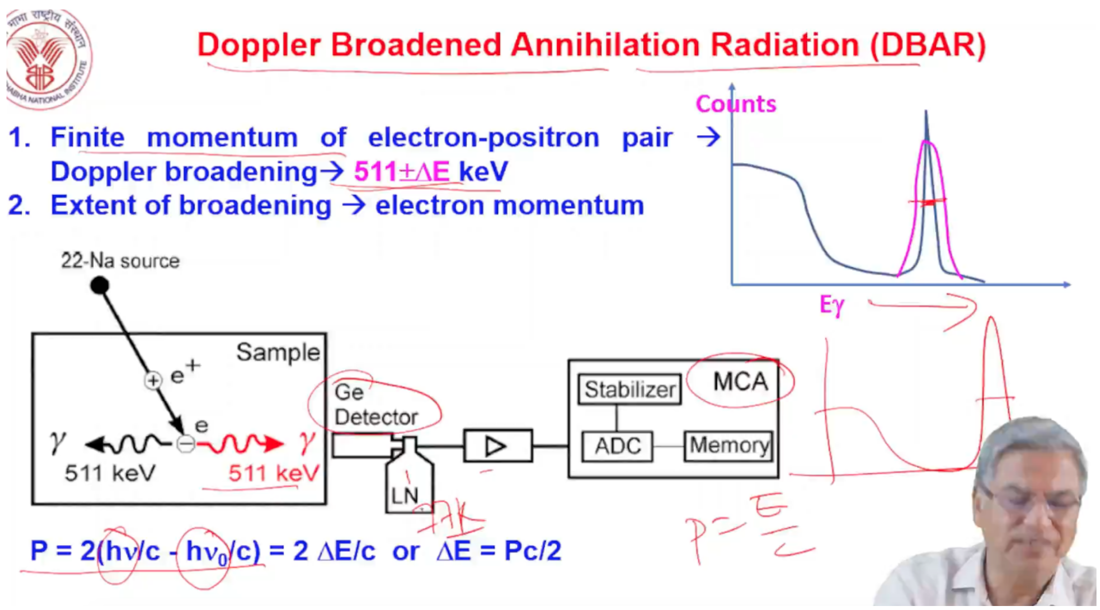
If you can determine the lifetime of positron, how do we determine the lifetime? The time between 1275 keV and 511 keV gamma rays. So I will explain the instrumentation for this lifetime measurement. So these are the three experimental techniques, the Doppler broadening of annihilation radiation, angular correlation between gamma rays and light time spectroscopy, which are used in positron annihilation spectroscopy. And other than this electron momentum and electron density measurements, another very interesting field is positronium chemistry. See the chemistry of positronium.

Positronium is an atom similar to hydrogen atom. In hydrogen atom you have a proton and an electron. Reduced mass of hydrogen atom is one mass of electron (m_e), reduced mass of positronium is ($1/2m_e$, (m_1m_2/m_1+m_2), $m_1=m_2=m_e$. And so accordingly, the binding energy or the ionization potential of the positronium is 6.8 eV, it is half of the hydrogen atom ionization potential, 13.6 eV. The radius of hydrogen atom is 0.54 A, the radius of positronium is 1.08 A. So double of the H atom, so you can see the beautiful chemistry of positronium atom. So when the positronium atom is formed, it consists of a positron and electron.

So depending upon the spins, if they are anti-parallel, you form a singlet state, anti-parallel spins of positron and electrons called singlet state or para-positronium. And this is the ground state of positronium and there is an ortho-positronium triplet state where both these spins are parallel. So this para-positronium has got a much shorter half-life of 125 picoseconds, which you can determine from this lifetime spectroscopic data. And this is disintegrating, this decays by two photons, that means two 511 keV gamma rays. So that is the normal positronium decay.

Whereas the ortho-positronium is a triplet state of positronium atom and in vacuum has got a lifetime of 140 nanoseconds, so very high lifetime. And since this has got a spin of one, though if it has to decay on its own, it decays into three photons, 1.02 MeV upon 3 roughly about 370 keV each photon. But what happens now? In 140 nanoseconds, it is very difficult, highly improbable that positronium will remain as an ortho-positronium. Before that it undergoes different types of reactions like pick-off, oxidation, spin conversion and so on.

And so you see an ortho-positronium signature in a higher life time component, instead of 125 ns, you may have 150, 200, 250 picoseconds life time. So this is another area in chemistry of positronium atom itself. These are the three techniques by which you can do studies with positron annihilation spectroscopy.



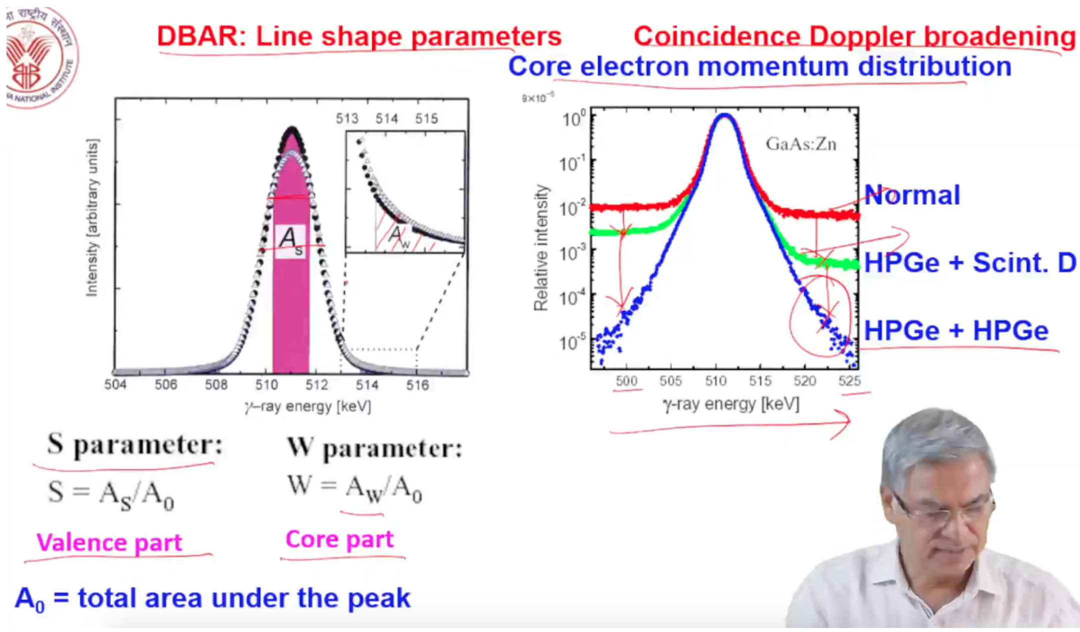
So let us discuss in more detail these experimental techniques of Doppler broadening and lifetime spectroscopy. As I mentioned, the finite momentum of the electron positron pair when the pair is annihilating leads to the Doppler broadening. Recall the typical gamma spectrum obtained using high purity germanium detector (HPGe). HPGe has got very high resolution. And so you will see that if you have a source emitting 511 keV gamma ray, not positron. The positron emitting source also gives 511 keV but there are sources which emit 511 keV gamma ray after the decay of the parent. So that gamma is much narrow. And so this is the inherent resolution of the detector for 511 keV. But because of Doppler broadening, if it is a positron, if this peak is due to the annihilation gamma ray coming from positron annihilation, then this peak becomes much broader. And it is significantly broader. It is not that you don't see it. In a gamma ray spectrum, if it is due to radioactive decay, you will see a much narrow peak at 511. If it is due to Doppler broadened positron annihilation, you will see a much broader peak.

And so if you can determine that by broadening of this 511 keV peak, you can study the electron momentum. So the instrumentation for this Doppler broadened annihilation is, we have a high purity germanium detector, it has to be cooled at liquid nitrogen temperature 77 K to reduce the leakage current. Then you have the pre-amplifier, amplifier and then you put it to the multi-channel analyzer through ADC and so on. So this MCA spectrum gives you the 511 keV gamma ray and it measures the width of, so instead of the width, you see different parameters, which I will explain in the next slide. And from this simple gamma ray spectrum with the setup, but it has to be highly stabilized gamma ray spectrum because you are looking for the broadening over 511 keV by few eV broadening, maybe 0.5 keV or so. How do you get the momentum of the electron? So the momentum of that photon is given by hν/c, momentum of the photon is

E/c. And so if hν_0 was the 511 keV and hν is the Doppler broadening, then you have hν/c-hν_0/c.

$$P = 2\left(\frac{h\nu}{c} - \frac{h\nu_0}{c}\right) = \frac{2\Delta E}{c} or\ \Delta E = Pc/2$$

You can determine, from the broadening, the momentum of the electron. That is the methodology for Doppler broadening.



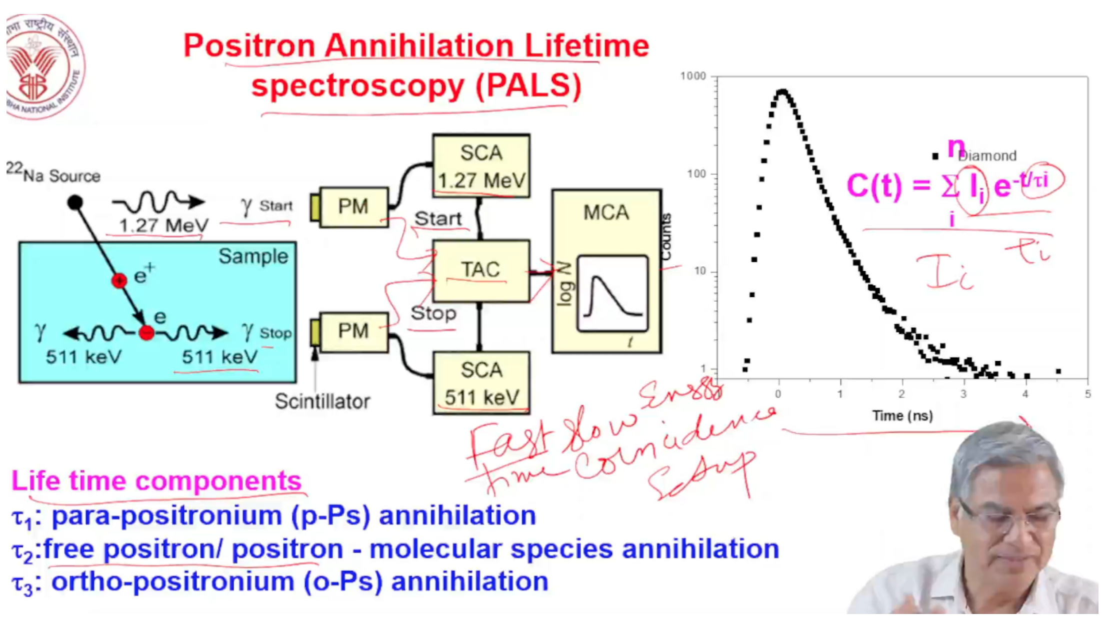
So in Doppler broadening, what is important is the line shape parameter. So this is a typical 511 keV gamma ray and you can see the 511 keV gamma ray FWHM will be here. So if the FWHM of a normal gamma ray is 1 keV, you will see it at 2 keV. You can see from 510 to 512. And so there are certain parameterization called S-parameter.

The S-parameter is defined as the width, the area under this graph up to certain width upon the total area. So the area of the pink shaded area upon the total peak area is called S-parameter. So essentially it tells you the momentum of the valence electron because these are the low momentum events. Whereas if you take the tail part of the 511 keV spectrum, this tail part expanded here and you take this parameter, then that area upon A_0 is called W-parameter, the Y part. And that gives you the momentum of the core electrons.

So you can try to get the valence electrons and core electron momentum from the Doppler broadening of annihilation radiations. In fact, from the normal DBAR experimental data, it's difficult to get the W-parameter because the W, this width is in the tail part, the wider part. So the tail, you may have the Compton due to other high energy gamma rays or there can be background, so background will be more. So if you can reduce the background by some technique called coincidence Doppler broadening, then you can have more accurate data about the core electron momentum. So here, this is again the Doppler broadening spectrum.

So this was the normal, this is the same as this spectrum where you just have an HPGe detector and record the gamma spectrum of 511 keV around that. We can see here 500 to 525 keV is the region of interest for the annihilation radiation. But what you do if you put a NaI(Tl) or scintillation counter in coincidence with the HPGe detector. So this particular spectrum is gated by a coincidence between two 511 keV, one 511 is measured in HPGe, and other one is just the other scintillation counter that will trigger this gamma spectrum. You can see there is a significant reduction in the background.

And on top of that, if you have two HPGe detectors and then you gate this Doppler broadening, in fact this 511 keV gamma, you will be coincident between the two HPGe detectors. If you gate this gamma spectrum, then you can see there is a significant reduction in the background. And then you can study, these are the core electron momenta because of core electron momentum. So you can obtain the core electron momentum distribution in the coincidence Doppler broadening. Normally a laboratory which is doing positron annihilation spectroscopy, will be having a coincidence Doppler broadening setup as well.



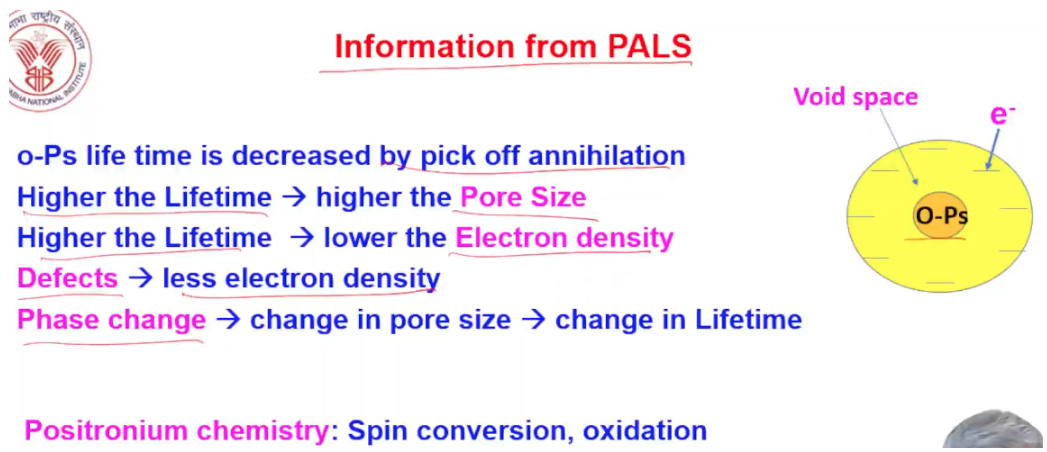
Another technique I was mentioning is the positron annihilation lifetime spectroscopy. And you measure the lifetime of a positronium or positron by a setup called fast slow coincidence setup, where this 1275 keV gamma ray from Na-22 source is triggering the start and the 511 keV are triggering the stop. So you have a circuit by means of which you determine the time difference between two gamma rays, 1275 and 511 keV. So what you do, you have a single channel analyzer where you gate the gamma ray 1275, another single channel analyzer you gate 511 keV gamma. And you take a start signal and a stop signal to time to amplitude converter (TAC).

The TAC converts the time to voltage signal. So the time gap between these two detectors for an event is converted into a voltage signal by TAC. And this TAC output is an analog output, which will get you the time spectrum. The x-axis is the time and y-axis is the counts. So this kind of a coincidence setup, it is called the fast slow coincidence setup.

So when we say fast means time signal, slow means energy. So you have one circuit for energy to gate the gamma rays 1275 and 511 keV. You have one circuit for timing, you have fast signals coming from the PMT of the two constant fraction discriminators, you put them into the start and stop signal and you get the tag output. Now, this output looks like this. You can see here, this is called the time spectrum, counts versus time.

What you get is a fast rise and slow exponential decay. That exponential decay shows multiple exponential decays. The counts are a superposition of maybe two or three exponentials. So every component has got an intensity I_1, I_2, I_3 and here τ, lifetime τ_1, τ_2, τ_3. So you can fit this data into multi exponential curve and get the constants I_i. So what you get the outputs as I_1, I_2, I_3, τ_1, τ_2, τ_3. τ_1 and its intensity is I_1. So what do these lifetimes represent? They are called lifetime components. This τ_1 is actually that 125 picoseconds that is the lifetime of the para-positronium. That is the shortest component. So when the para-positronium annihilates, you get 125 picosecond.

So the first shortest component will be para-positronium annihilation. And it does not really give you any chemical information because time is too short. The second one is the τ_2 more than τ_1, you have τ_2 and it tells you the free positron or positron molecular species annihilation. So it is usually actually a sort of a pick up reaction. The positronium can interact with the molecular species and undergo changes. So that will increase the life time. When the positron is binding with the molecular species, lifetime will increase and that gives you information about the chemical species that is formed. And third is τ_3, that is the ortho-positronium annihilation. Ortho-positronium lifetime is 140 nanoseconds, but this τ_3 is not 140. It will be a few nanoseconds. So you have 125 ps, another one maybe 150 to 200 ps, something like that. And τ_3 is the longest life time component. That can vary depending upon the type of material that you have.



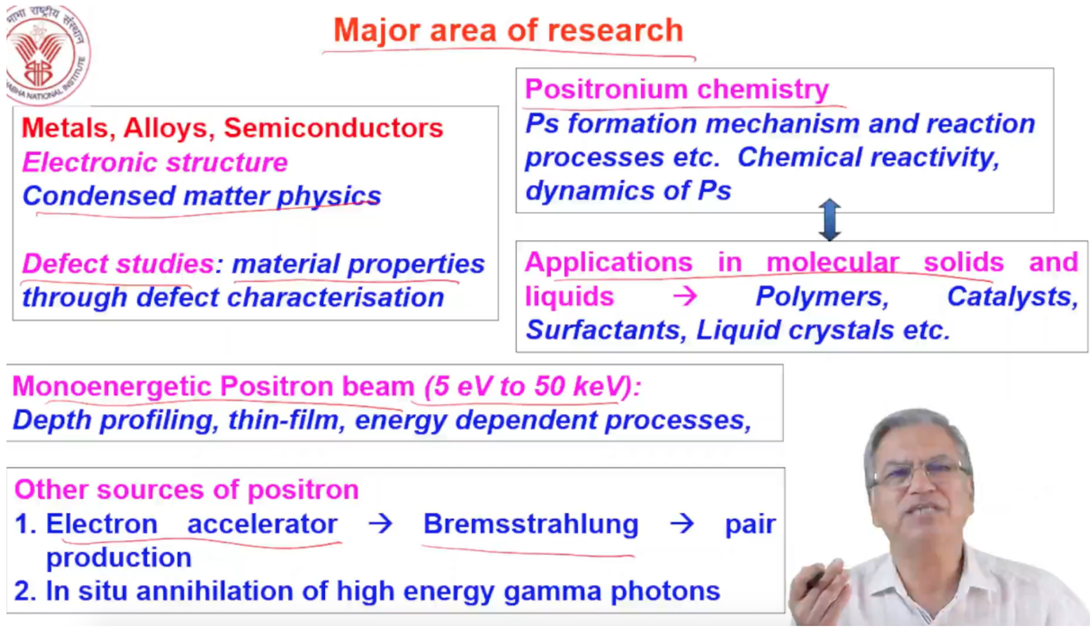
So what information you get from positron annihilation, life time ? The ortho-positronium lifetime 140 nanoseconds decreased by pick off annihilation. That means when you have an ortho-positronium where both electron-positron spins are parallel, it can pick off, this electron can be picked up by chemical species and it will annihilate with another electron. So this essentially tells you the electron density or, suppose you have a zone in which there are not many electrons, the positronium will survive for more time.

So the ortho-positronium lifetime depends upon electron density. If electron density is high, lifetime is short. If lifetime is high, electron density is low. So like a defect, there are no electrons in that defect site. So positronium will go and sit there. It will prefer to stay in its site where there are not many electrons.

Like in metals, you don't see r_3, you only see r_1. So it tells you about the electron density or even pore size. In polymers, when there are pores, the polymers will have areas having pores, it can be open or closed. And the positron has a tendency to go and sit in the pores so that it can survive longer. And so the lifetime essentially tells you the pore size. Defects sites, wherever the electron density is less, that means it is a defect, defective site.

So it will give you the defect concentrations. And the phase change in terms of polymers, you know, if there is a change in the polymer pore size, it is going to be a phase change, then it can tell you about the pore size. The change in pore size or essentially phase change. Like certain plastics, plastic materials can undergo changes so that it can tell you about different phases. That's like glass transition in plastics can be monitored. And of course, the positronium chemistry also can be studied, positronium can undergo oxidation.

The electron is taken up by the metal ion and you have a positron. Similarly, it can undergo spin conversion with another chemical species. So positronium chemistry itself is a subject. There are books on only positronium chemistry. So you can refer to, if you are interested in doing research in positronium chemistry or positron analysis, one can go to the literature and read the books.



So what are the areas in which one can do research using positrons? The major areas of research include solid-state, condensed matter physics. We can study positron annihilation spectroscopy in metals, alloys, semiconductors to determine their electronic structure. Like if you are determining what are the bands due to, in the metals and semiconductors, we have the different bands overlapping. Which electrons are participating in these bands? You can study the momentum of electrons by Doppler broadening of annihilation radiations. If you are going to study defects, you can go to life time spectroscopy and that essentially the defects will dictate the properties of materials. So you can analyze the properties of materials through characterization of the defects.

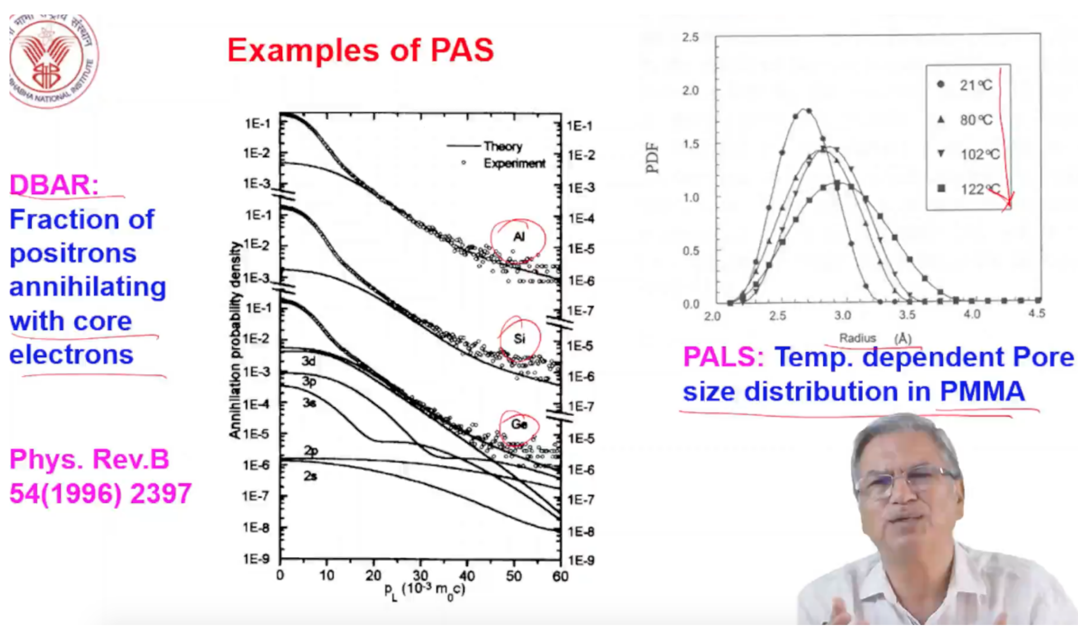
So in fact, defects play a big role in governing the properties of different types of material. They can be optical property, electrical properties and so on. So this is a vast area where you want to study defects by using lifetime microscopy. And you have the positronium chemistry, the positronium atom formation mechanism, how the positronium is being formed in different materials, like, for example, water and benzene. You would find that the positronium formation is different in water and benzene.

And their reaction processes like what is the chemical reactivity of positronium atom towards different species and the dynamics of the positronium atom formation. And this is associated with the applications in molecular solids and liquids. So is another area where you can study the structures of polymers, catalysts, surfactants, liquid crystals and so on. Wherever you will find that the molecular arrangement in the sample is going to change, so that will affect either the pore size or electron density. So that will affect the positron lifetime.

Now there have been several advancements in the techniques of positronium annihilation. So there are now positron beams from the ^{22}Na. Whatever positron is coming out, you can analyze and then accelerate to the required energy. So you can have monoenergetic positron beam of energy 5 eV to 50 keV. And this positron of monogenic energy can be used in depth profiling of defects, characterization of thin films, etc.

So whenever there is an energy dependent process, you can do the study using monoenergetic positron beams. It is not that you have only ^{22}Na as a source of positron. You can have ^{64}Cu in a reactor or you can have positron from electron accelerator. You can stop the electrons in a high Z material, produce Bremsstrahlung, and thereby pair production which will give you positrons.

Or you can have positrons generated in-situ. Suppose you have a high energy gamma ray produced in a nuclear reaction, and you stop that gamma ray in your material of interest, then in-situ that gamma ray will produce positrons via pair production, and the Doppler broadened annihilation 511 keV gamma spectrum you can use to find out the electron momentum in the machine. So a lot of high technology materials have been also studied using the in-situ, the positron annihilation spectroscopy using in-situ gamma ray.



So just to give you examples of positron annihilation spectroscopy, by Doppler broadening, as I mentioned, you essentially get the momentum of electrons. And if you do coincidence Doppler broadening, you can do momentum of core electrons. So you can see the fraction of positrons annihilating with core electrons by coincidence Doppler broadening can be obtained for different metals, aluminum, silicon and germanium.

You can study all types of metals, how the positron is annihilating with core electrons and valence electrons. So the role of core electron, valence electron in positron annihilation can be studied. And by this you can actually characterize an element by the core electron momentum. So suppose you have a sample, from the core electron momentum you can index the metals, Z of the particular element you can index.

And another example is the lifetime, from the lifetime spectroscopy, you can find out the pore size distribution. This is the radius of the core. So certain materials like, you know, like poly methyl methacrylate is a polymeric material, which will undergo changes in the pore size distribution with temperature. And you can see the pore size distribution is changing with the temperature. So how the polymeric material is undergoing changes, the internal transitions in the polymeric material can be investigated by pore size distribution study using lifetime spectroscopy. So these are just to give you examples of what you can do, but you can take a topic and see how positron annihilation can be utilized in the study of a particular topic.

So there is a vast area of research using positron annihilation spectroscopy. So I will stop here and take up the next part in the next lecture. Thank you very much. Thank you.