

Nuclear probes: Perturbed angular correlation

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Lecture-19, Module-2

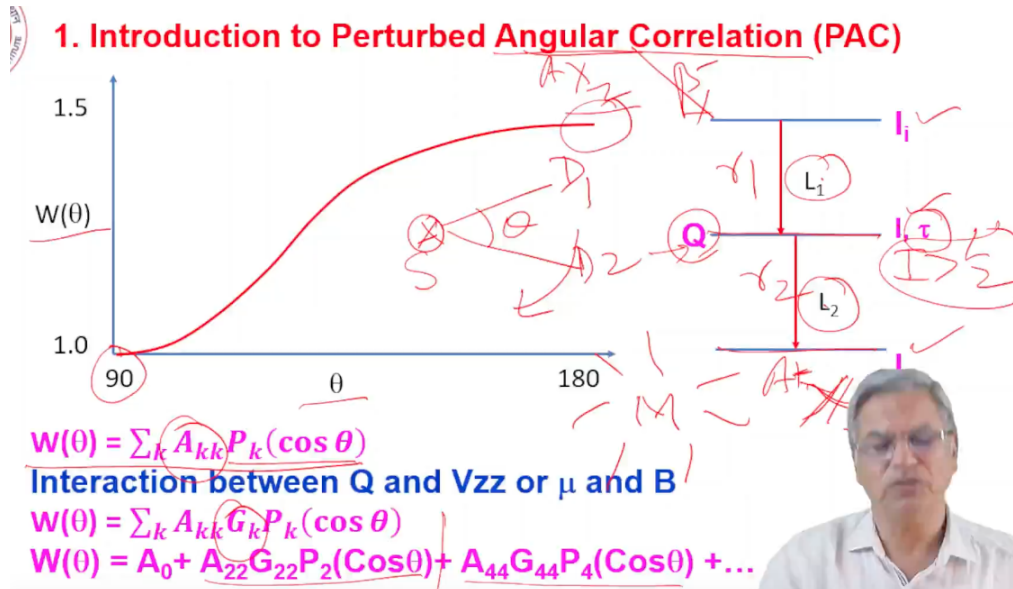
Hello everyone. In the previous lecture, I introduced a topic called positron annihilation spectroscopy, which is a nuclear probe technique to study electron momentum distribution and also the defects or pore size in different types of materials.

Now, I will discuss another technique, which is another nuclear probe technique. In fact, this is more like Mossbauer spectroscopy, wherein we study the angular correlation between two gamma rays and determine the electric field gradient, electronic environment in different types of materials.

Perturbed angular correlation (PAC)

1. Introduction to PAC ✓
2. Theory of PAC ✓
3. Instrumentation for PAC ✓
4. Characteristics of a PAC probe ✓
5. Applications of PAC

So, in this particular lecture, I will introduce the topic of perturbed angular correlation (PAC), then the theory behind the PAC, what is the instrumentation for PAC, what are the requirements for a particular radioisotope to be used as a probe for PAC and some of the applications of PAC.



Okay, so just let me introduce what is the technique of perturbed angular correlation. First let us first understand the angular correlation between two gamma rays. Suppose you have an isotope undergoing beta minus or beta plus decay. So, $^A X$ goes to $^A Y$ by β^- .

So, this particular decay scheme is for a beta minus emitting radioisotope. And if it has got a cascade of gamma rays, so you have gamma one, you have gamma two, the gamma ray will have their own multipolarities like magnetic dipole, electric quadrupole and so on. These are the spin states of the three levels, the ground state and the excited states. Then these gamma ray, these two gamma rays will have a definite angular correlation between them. What I mean by angular correlation? We have a source here and you put two detectors at a particular angle and you vary this detector and measure the coincidence counts.

So, this is what we are going to measure called angular correlation. As a function of theta, you will find the coincidence counts between these two detectors are not same. Depending upon the spin states of the three levels, you may have low counts at 90 and higher counts at 180 or vice versa. It depends upon the angular momentum of the spin states and the multipolarity of the gamma rays. So, this is called the angular correlation and this angular correlation is used in finding out the spin states and multipolarities of the gamma rays.

The expression for this angular correlation function $W(\theta)$ is given below.

$$W(\theta) = \sum_k A_{kk} P_k(\cos \theta)$$

A_{kk} are called the directional correlation coefficients. They are the 3j symbols, the Clebsch-Gordon coefficients between I_i L_1 , I for one first radiation, I , L_2 , I_f for the

second transition. So, that one can actually calculate using angular momentum coupling and $P_k(\cos\theta)$ is the Legendre polynomial of k th order. So, this is the general angular correlation between two gamma rays. But if you have certain conditions in a probe, that is the intermediate level has got a lifetime more than about one nanosecond and it has got a spin more than half, then it will have finite electric quadrupole moment.

So, these are the two conditions. The intermediate level should have spin more than half, so that it has got a quadrupole moment and it has got a lifetime (τ) of the order of nanoseconds. Normally lifetime will be in picoseconds, so then it is of no use. With these two conditions, you will find that the electric field gradient around this, suppose you have a metal atom and you have this coordinated to different ligands and you have a crystalline matrix. So the ligands offer a certain electric field gradient around the metal ion.

If it is non-cubic, then this electric field gradient will interact with the quadrupole moment to perturb this angular correlation. And this perturbation of angular correlation leads to perturbed angular correlation and this perturbation factor is called G_k .

$$W(\theta) = \sum_k A_{kk} G_k P_k(\cos\theta)$$

So the angular correlation is perturbed because of interaction of the quadrupole moment of the intermediate nucleus with the surrounding electric field gradient. It can also change by interaction of the magnetic dipole moment of the nucleus with the surrounding magnetic field. There are magnetic materials, so they are the magnetic dipole moment will come into picture.

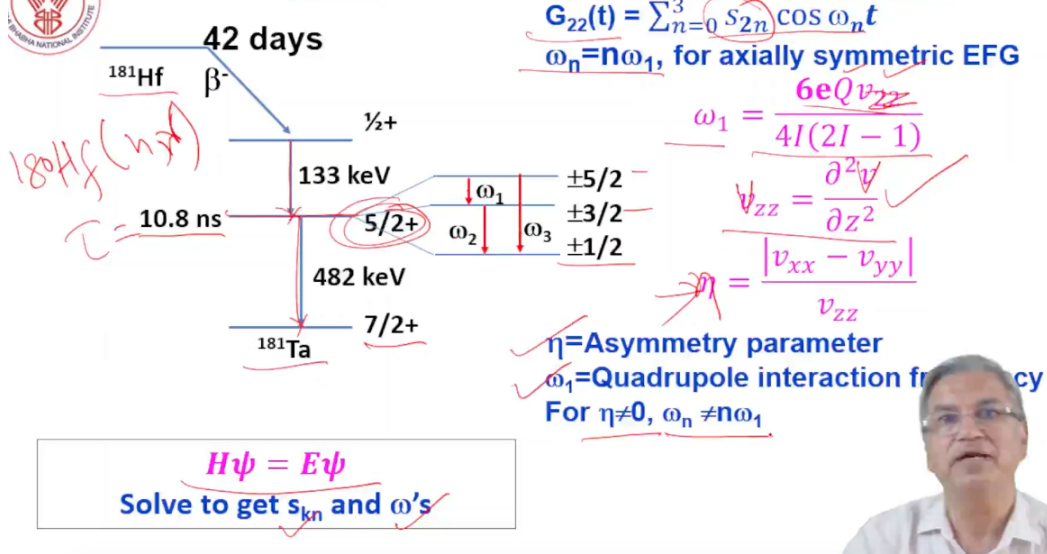
Now you can expand this legendary polynomial.

$$W(\theta) = A_0 + A_{22} G_2 P_2(\cos\theta) + A_{44} G_4 P_4(\cos\theta) + \dots$$

So normally we will take up only the second order term. This fourth order term also is important, but we require a little more elaborate arrangement.



2. Theory of PAC



So let me go into little more details about the theory of perturbed angular correlation and try to give you an example of a probe atom which is a suitable radioisotope for perturbed angular correlation.

^{181}Hf you can produce by $^{180}\text{Hf}(n,\gamma)$ and this ^{181}Hf undergoes beta minus decay, with the half life of 42 days to the excited states of ^{181}Ta . So $\frac{1}{2}^+$ state decays by 133 keV gamma ray, it goes to $\frac{5}{2}^+$ state and by 482 keV gamma ray it goes to $\frac{7}{2}^+$ state of ^{181}Ta . Now you can see here this intermediate state has a life time (τ) of 10.8 nanosecond and has got a spin of $\frac{5}{2}^+$. So it has got all the nuclear parameters which makes it conducive for PAC as a probe.

So what happens? When this hafnium is put in an asymmetric electronic environment like non-cubic geometry, you have orthogonal, orthorhombic, monoclinic type of geometry, then in that lattice positions, they will offer a non-cubic environment around the metal ion and so this non-cubic environment will have certain electric field gradient. So this electric field gradient I have explained here, this will interact with the electric quadrupole moment of the nucleus in its intermediate state and split this intermediate level into its magnetic sub levels. So you have the splitting in electric field gradient as $\pm 1/2$, $\pm 3/2$, $\pm 5/2$. Unlike in NMR, in NMR each magnetic state is split separately. So you have $\frac{1}{2}$ state split into $+1/2$ and $-1/2$.

So magnetic splitting of this level will give you six separate levels, $\pm 1/2$, $\pm 3/2$, $\pm 5/2$. But electrical interaction splitting will give you only three levels. So when you have first gamma emitted to this, they are populated in a certain way. So when we say perturbation of angular correlation, essentially the population of this magnetic sublevels had changed

because of that perturbation. So essentially what we have to do, you have to solve the Schrodinger equation for the quadrupole interaction or magnetic interaction.

You have to have the Hamiltonian containing the quadrupole moment and the electric field gradient or like you say $\mu.H$ for NMR. Similarly $Q.V_{zz}$, this quadrupole moment and electric field gradient are tensor quantities. So you have to solve the Schrodinger equation to get the eigenvalues and their amplitudes. So you have the transitions among these magnetic sublevels, $\omega_1, \omega_2, \omega_3$ and their amplitudes are S_{kn} coefficients. So we have here the angular correlation function

$$W(\theta) = A_0 + A_{22} G_2 P_2(\cos\theta) + A_{44} G_4 P_4(\cos\theta) + \dots$$

where G_2 is the perturbation factor which is given by,

$$G_{22}(t) = \sum_{n=0}^3 S_{2n} \cos \omega_n t$$

S_{kn} coefficients are the amplitudes of the frequencies (ω_n) with $\omega_n = n\omega_1, n = 1, 2, 3$ for symmetric EFG. If the electric field gradient is axially symmetric, axially symmetric means this η value, the asymmetry parameter is 0, we say EFG is axially symmetric, that is $V_{xx} = V_{yy}$. In that case, these ω values are integral multiples of ω_1 , that is $\omega_2 = 2\omega_1, \omega_3 = 3\omega_1$. In that case, the frequency can be given as,

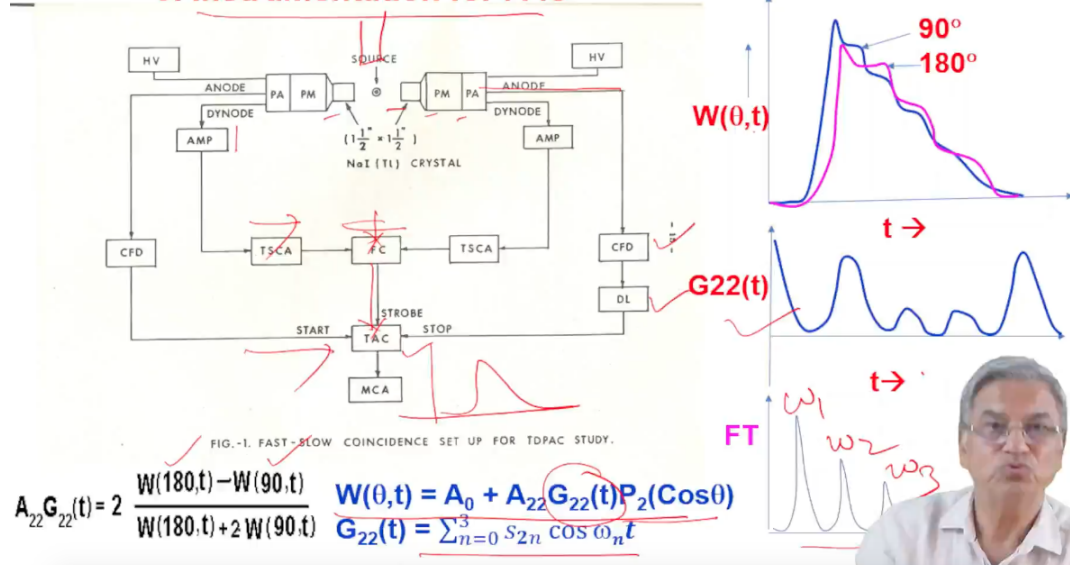
$$\omega_1 = \frac{6eQV_{zz}}{4I(2I-1)}$$

where V_{zz} is the second derivative of the electric field gradient, that is $\partial^2 V / \partial z^2$.

So essentially what you are getting is the electric field gradient V_{zz} , if it is axially symmetric and if it is axially asymmetric, then you get this parameter, asymmetric parameter (η), which tells you what is the asymmetry in the electric field gradient. So finally, the parameters you get out of PAC are asymmetry parameter and quadrupole interaction frequency.

If its asymmetry parameter is not 0, that means if it is not axially symmetric, then the ω_n 's are not integral multiples of ω_1 , they are dependent upon the η . So this was the theory of PAC. You can go through the book on PAC and understand more of it.

3. Instrumentation for PAC



Now the instrumentation for PAC is similar to the positron lifetime spectroscopy. You have to have actually three detectors. I have shown two detectors. The NaI(Tl) detectors can be used. So one and a half inch by one and a half inch NaI(Tl) coupled to PM tube and the preamplifier. Then you take the anode output for timing and through a set of constant fraction discriminator and delay that becomes the start signal of the time to amplitude converter and same is for the stop side. For energy you take the dynode output for amplifier, gate the gamma ray in here and you generate the fast coincidence signal from here.

This fast coincidence will strobe the TAC, what you get in the MCA, you gate the time spectrum of MCA and you will have, if you have one more detector here, then you will get two time spectra, one for 90 degree or one for 180 degrees. So basically you require to get this $W(\theta)$ as a function of time. Since you are doing time differential PAC as a function of time, you record the time spectra and then you will see on the normal exponential there will be oscillations because of that perturbation. So this you fit into the function

$$W(\theta, t) = A_0 + A_{22} G_{22}(t) P_2(\cos \theta)$$

$$G_{22}(t) = \sum_{n=0}^3 S_{2n} \cos \omega_n t$$

So there are standard software available. If you feed the data of 180 and 90 degree coincidence time spectra, you can get the Fourier transforms directly. So you essentially get ω_1 , ω_2 like in FTNMR you get directly the frequency. Similarly, here also you can get

the, like the FTNMR you get the data by Fourier transform. Fourier transform of time domain spectrum will give you the frequency domain.

So what essentially you do, you have the counts at 180 degrees, you have the counts at 90 degrees and if you recall the $P_2(\cos\theta)$ is nothing but $\frac{3}{2} \cos^2\theta - 1$. So you can substitute for two angles the value of $P_2(\cos\theta)$, you can get G_{22} . So you require two angle data to find out $G_{22}(t)$ because you have A_0 and $A_{22}G_2$. A_{22} value is known, A_{22} is -0.49 for ^{181}Hf or the cascade of $\frac{1}{2}^+ \rightarrow \frac{5}{2}^+ \rightarrow \frac{7}{2}^+$ states.

So from this experimental data you can get this frequency data. So you need to get $F_1, F_2, F_3, \omega_1, \omega_2, \omega_3$ and you will also get the η parameter from the fitting of this G_{22} data. In fact, the ratio of $\omega_2/\omega_1, \omega_3/\omega_1$ will also give you the η .

4. Characteristics of a PAC probe

1. Long half life (few hours to few days)
2. Intermediate level spin ($I > 1/2$ for quadrupole interaction)
3. Intermediate level life time ($\tau > 1$ ns (resolving time ~ 500 ps)
4. Energy of gamma radiations in cascade: ≥ 100 keV
5. Chemical compatibility with host matrix

So let us see all the radioisotopes that you have, they are not amenable for PAC. There are few radioisotopes which can work as a PAC probe. Let us see what are the characteristics. Firstly, of course the half-life should be long enough, maybe few hours to few days so that you produce it in the reactor or accelerators, bring it to your laboratory, put it in the system, that is, your PAC setup and acquire the data. So your data acquisition may take few hours or a few days depending upon the statistics that you want to acquire. Then second is the intermediate level spin should be more than half for quadrupole interaction. Intermediate level lifetime should be more than a nanosecond.

Why this nanosecond lifetime? Because the resolving time of the instrument, when the two gammas are coming instantly, then the time resolution of the setup is of the order of 500 picoseconds. So your lifetime should be more than the resolving time of the equipment so that the exponential decay of the level can be seen on the life time spectrum. Then the energy of the gamma rays in cascades should be more than or about 100 keV or more. Because at less than 100 keV the window of detector will start attenuating the gamma ray. And of course the probe should be compatible to the host matrix.

So if you are studying hafnium as a probe, all these rare earths or even titanium zirconium compounds you can study. So you could see the radii or the chemistry, valency should match with the one of the elements in the sample.

parent	half-life	decay	isomer	half-life (ns)	$E(\gamma_1)$ (keV)	$E(\gamma_2)$ (keV)
⁶² Zn ✓	9.186(13) h ✓	EC/β ⁺ ✓	⁶² Cu ✓	4.57(18) ✓	596.56(13) ✓	40.84(3) ✓
⁹⁹ Mo ✓	65.94(1) h	β ⁻	⁹⁹ Tc	3.61(7)	739.50(2)	181.0939(19)
^{111m} Cd ✓	48.54(5) min	IT	¹¹¹ Cd	85.0(7)	150.82(2)	245.42(1)
¹¹¹ In ✓	2.8049(1) days	EC	¹¹¹ Cd	85.0(7)	171.28(3)	245.42(1)
¹¹¹ Ag ✓	7.45(1) days	β ⁻	¹¹¹ Cd	85.0(7)	96.73(8)	245.42(1)
¹³³ Ba ✓	10.52(13) years	EC	¹³³ Cs	6.27(2)	356.017(2)	80.997(2)
¹⁶⁰ Tb ✓	72.3(2) days	β ⁻	¹⁶⁰ Dy	2.02(1)	197.0352(10), 879.383(3), 1177.962(4), 1271.880(8)	86.7882(4)
¹⁸¹ Hf ✓	42.39(6) days	β ⁻	¹⁸¹ Ta	10.8(1)	133.024(17)	482.182(23)
^{199m} Hg ✓	42.6(2) min	IT	¹⁹⁹ Hg	2.45(2)	374.1(1)	158.37950(9)
^{204m} Pb ✓	67.2(3) min	IT	²⁰⁴ Pb	265(10)	911.78(7)	374.72(7)
isotopes that have only been used for the sum-peak method						
¹⁴⁷ Nd ✓	10.98(1) days	β ⁻	¹⁴⁷ Pm	2.50(5)	439.895(22)	91.10(2)
¹⁵² Eu ✓	13.542(10) years	EC	¹⁵² Sm	1.428(7)	841.586(8)	121.7825(4)

So you can see here, this is the list of radioisotopes, the parent isotopes which you have to produce in the reactor, the half-lives, what the mode of decay, what is the daughter product, the half-life of intermediate level lifetime and the two gamma rays which are in cascade. You can see Zn-62, Mo-99, Cd-111m, In-111, Ag-111, Ba-133, Tb-160, Hf-181, Hg-199m, Pb-204m, Nd-147, Eu-152. So these are the kind of radioisotopes which one can use.

So chemistry of elements containing these isotopes, these elements can be studied by, and sometimes you know like indium, it will go very well in the rare earth. Any trivalent metal ion, you can use indium as a probe. So that kind of analogy you can use to study different types of matrices.

5. Applications of PAC

1. Phase transitions in solids ✓
2. Radiation effects on solids ✓
3. Binding site of metal ion in biomolecules ✓
4. Diffusion in solids
5. Metal ion complexation and polymerization

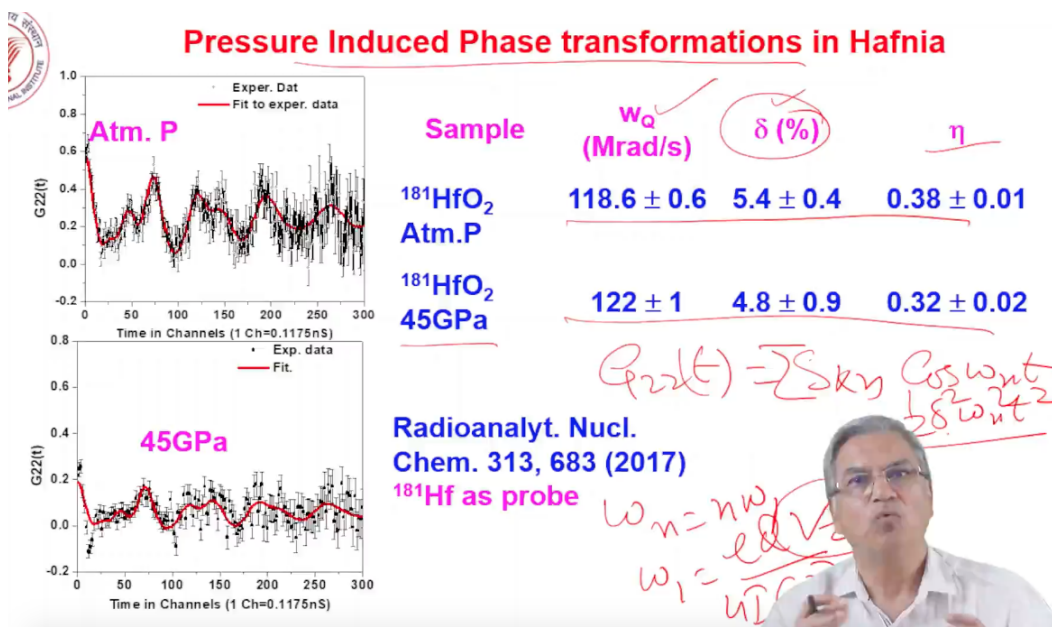
So let us see what are the areas in which you can apply PAC technique. So you can use PAC in studying the phase transitions like you know, if you start with the orthogonal,

orthorhombic matrix and it undergoes phase transition to monoclinic or triclinic, there will be change in the EFG.

So any phase transition where there is a structural change or there is a magnetic transition, you can study by TDPAC. And the sample remains intact except that you are introducing some radioactive isotope. You can study radiation effects in solids. Radiations you can introduce, maybe they may introduce defects or if you take an amorphous material, it may generate crystallinity or if you have a crystalline matrix, it may generate amorphicity or it can be even polymerization, it can lead to change in the molecular weight. So wherever there is a change in the chemical environment by radiation, you can study by TDPAC.

The binding site of metal ion in biomolecules, in fact in biochemistry, people are interested in knowing like you have a big molecule, protein molecule, where is that this metal ion is going to attach to this big molecule. So what is the geometry around that you can study by using TDPAC.

Another area is diffusion in solids. So for example, hydrogen diffusion in different materials. So when you have a material like palladium which absorb hydrogen, even zirconium absorbs hydrogen. So when the hydrogen is going in the material, it may be diffusing out and during the diffusion, there is a change in the electronic environment around the probe atom and the change in the electronic environment can be probed by using TDPAC. Complexation of the metal ion and the ligand or polymerization of the metal ions can be also studied using TDPAC. So I will just give you some examples of perturbed angular correlation.



One of our colleagues has studied what we call as the phase transitions in hafnium oxide as a function of pressure, at high pressure, hafnium oxide undergoes changes. So that kind of study you can do. So if you have hafnium oxide irradiated in the reactor and at atmospheric pressure, you study the TDPAC. You can determine the parameters like quadrupole interaction frequency. In fact, I forgot to tell you about this δ part. The perturbation function formula,

$$G_{22}(t) = \sum_{n=0}^3 S_{2n} \cos \omega_n t$$

is for a system which is perfect. There is no fluctuation in the electric field gradient. But if the ω is changing, so the electric field gradient is changing. What is ω ? ω_n can be $n\omega_1$. And this ω_1 is,

$$\omega_1 = \frac{6eQV_{zz}}{4I(2I-1)}$$

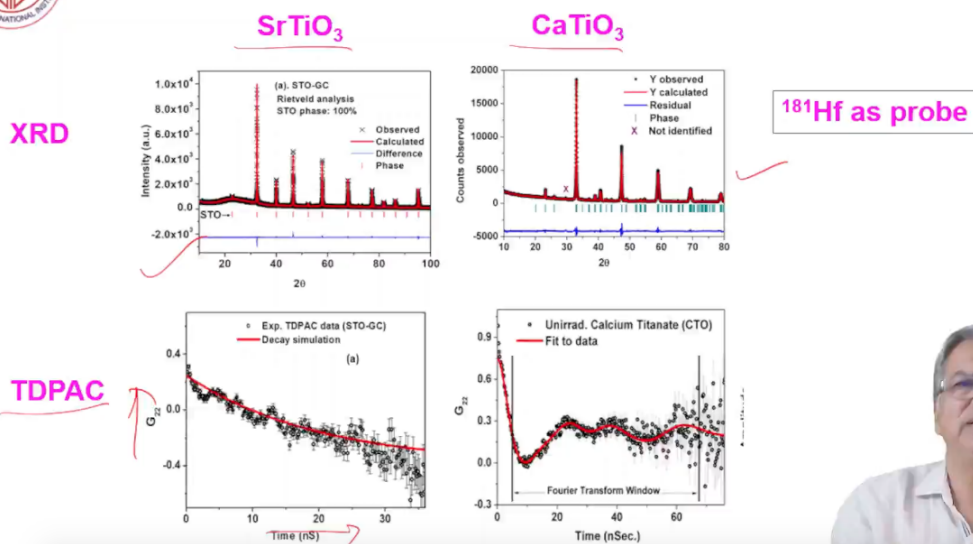
So this electric field gradient if it is changing, suppose the metal ion is not sitting in the same environment everywhere, then there will be a distribution of frequencies.

And that distribution of frequencies will give you $-1/2\delta^2\omega_n^2t^2$. So this is like you can use a Gaussian distribution of frequencies. So this δ is the distribution in the frequencies as percentage. What is that? Like 0.054 ω . So then this is the fluctuation in the electric field gradient.

So what my student did in the present work. At atmospheric pressure, this is the kind of data you get. And then you apply, you put this hafnium oxide in a diamond anvil cell and then study. So at 40 to 45 GPa, you can see that the quadrupole interaction parameters, the frequency, the δ value and the asymmetry parameter have been changed significantly. So you can carry out this study as a function of pressure and see what type of geometry that it is changing when you apply pressure. So pressure induced phase transitions can be studied by means of this technique.



Radiation effects on solids



Similarly, the radiation effects in solids can be studied by TDPAC. The radiation effects in solids, one of these studies was recently carried out is perovskites, strontium titanate and calcium titanate. They are being investigated as a host matrix for the waste that is generated in the reprocessing of the spent nuclear fuel. And therefore, a lot of materials are being investigated for that they can be used to accommodate the fission products and minor actinides and then for final disposal in a repository. So this by gel combustion method, they were synthesized. And so first you characterize them by X-ray diffraction and dope hafnium- 181, a probe.

So the doping concentration should be of the order of 0.1% to 2.5% so that you don't alter the crystalline structure very much. And of course hafnium can go and sit in the place of titanium as their ionic radii are very close. Then after you dope, maybe you can anneal also or you can dope while preparing the compound and then study the time differential perturbed angular correlation.

So PAC and TDPAC, the difference is that in TDPAC, you are recording the time spectrum. So this TDPAC is essentially PAC only. And you can see as a function of time in nanoseconds, the G_{22} , in the case of strontium titanate, it is a cubic lattice. So it is supposed to have no EFG, but even then you get some static interaction. And in calcium titanate, you get a well-defined EFG. So after this, now you can study the EFG and then once you irradiate with the different radiations like gamma rays or electrons or alpha particles, then one can study effect of radiation. Essentially, you irradiate at a particular dose and determine the quadrupole interaction parameters, the frequency ω , the distribution of frequency δ and the asymmetry (η) of the electrical field gradient.



Biological applications

Binding site coordination geometry of Carboxypeptidase

Solution form →

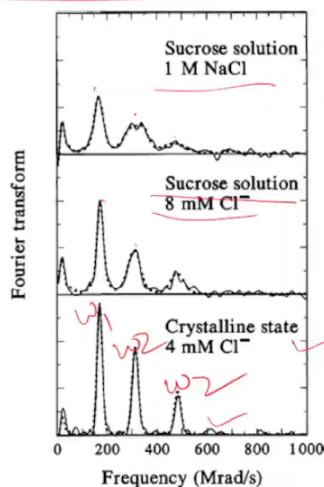
2 NQI

dynamic exchange
between two binding
sites

Crystalline form →

1 NQI

Biochemistry 1997, 36,
11514



¹¹¹Cd as probe



Similarly, the biological applications, very interesting studies can be done in biology where the particular metal ion is going to bind the big macromolecule. So one of the studies I have taken from the literature is the binding site coordination geometry of carboxypeptidase. And what essentially they have done that they have used ¹¹¹Cd as a probe nucleus and this ¹¹¹Cd was doped into this material. So it is essentially not as a doping, it is going to bind. This cadmium will bind the carboxypeptidase in the particular geometry and what is the coordination environment around cadmium one can study using TDPAC..

What they found that when the carboxypeptidase is in the crystalline phase, in the crystalline phase they found that there is only one, what we call as the, nuclear quadrupole interaction (NQI). The nuclear quadrupole interaction is essentially nothing but the interaction between the quadrupole moment and the electrical gradient. So this is also called as the NQR, nuclear quadrupole resonance like Mossbauer spectroscopy. So here it is nuclear quadrupole interaction or we can also call it hyperfine interaction because the intermediate level is split into its magnetic substrates. So what they found that in the crystalline form you get distinct frequencies, ω_1 , ω_2 , ω_3 and one can find out the electric field gradient and match with the X-ray data.

But what they found is that when you try it in the solution form they found like particularly sucrose solution at different chloride concentrations, one molar sodium chloride and 8 millimolar chloride ion. Then they found that these peaks have become broad. You can see the peaks have become broad here also. So why these peaks get broadened? Because if there are two sites, so cadmium is sitting in sites mean, there is a fluctuation in the electric field gradient around cadmium and that can happen if there are

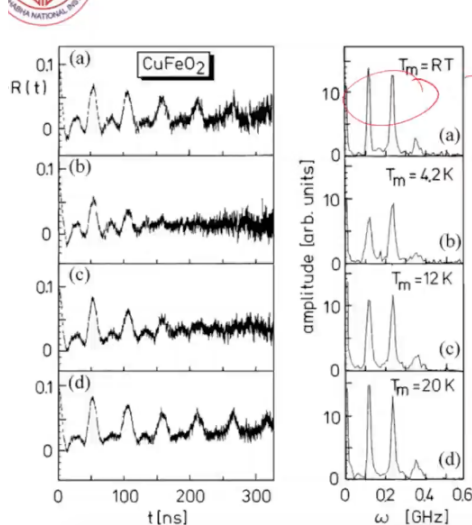
two sites. So some cadmium ions are sitting in one geometry, other cadmium ions are in another geometry.

So there is a dynamic exchange between two binding sites like Tautomerism. Now how to find the time scale of that exchange? If it is a single peak then it is a much shorter time scale. If there are two peaks you see, then it is happening at a longer time scale than the TDPAC.

TDPAC see time scales are observed around, let's say, picoseconds. That is the kind of difference because the resolving time of TDPAC setup is observed around 500 picoseconds. So any event which happens at that time scale then you may not resolve it. But that may lead to broadening of the TDPAC spectrum. So the reason for the two sites could be like hydrogen bonding between two species, two groups in the molecule can lead to two different geometry around the metal ion. So this kind of studies have been seen in TDPAC and then we can explain their behavior, why these structures are changing, what is happening in the structure under those chemical conditions.



Phase transitions



PAC Measurements in 2D Spin-Frustrated CuFeO_2

M. Uhrmacher et al., Phys. Rev Letters 76, 4829 (1996)

Powder neutron diffraction \rightarrow two magnetic Xns at 16 K and 11 K.

TDPAC using ^{111}In as a probe

Combined electric and magnetic interaction.

Weak component broadens frequencies of the strong component



Another really interesting example in the literature in the phase transitions is on what we call as the spin frustrated copper ferrites. So this copper ferrites actually they have lot of applications and the powder neutron diffraction of this material showed two magnetic transitions at very low temperature 11K and 16K. So you can see what they have done that they wanted to know what are the kind of geometries. So neutron diffraction will give you that there are two transitions taking place.

Now you want to go for further investigation. So using ^{111}In as a probe, they wanted to know what kind of structures, what kind of interactions they are. So it's a magnetic material and if there is a non-cubic geometry there will be electric interaction as well as

magnetic interaction. So there is a combination of electric and magnetic interaction. So by electric field gradient interaction with quadrupole moment, you have this like splitting of $5/2$ into $\pm 1/2$, $\pm 3/2$, $\pm 5/2$ and if you have a magnetic field, it will split each one of them into its magnetic sublevels. So you have six levels now. So the combined electric and magnetic interaction can be studied by means of TDPAC. So what they found that, for example, you have the room temperature data and somewhere at 4.2 K, there is a broadening in that. So this 11K is somewhere in the middle of the two and so they essentially tried to study, when there is a transition. So there is a phase transition between these materials. What is happening to the structure? The structure could change or there could be change in magnetic ordering because of the magnetic interaction. So this interplay between the electric and magnetic fields can lead to this phase transition. So what they essentially found that the weak component between the two electric and magnetic was going to broaden the frequencies of the stronger component. So these are the kind of studies people have carried out using TDPAC.

So there are innumerable examples one can take up. I just wanted to illustrate that if you know the fundamentals of TDPAC or positron annihilation spectroscopy and if you are working in an area where the special information you want, then by setting up these instrumentations, you can go for studying the processes, chemical environment around the metal ions and it requires the knowledge of nuclear instrumentation. So you require to have the proper knowledge of detectors, the energy resolution, time resolution. If you set up the system and have a good data acquisition system, then you can study different areas in physics or chemistry. So that is what was the purpose of these lectures that it induces you to take up the nuclear chemistry, what are the areas in which one can take up research problems for investigation and they are not done in isolation. If we have TDPAC set up or a Positron annihilation spectroscopy setup, these are already, you know, you need to have the complementary information from other techniques.

So you combine the information from other techniques like XRD or other techniques and use this data to obtain a complete picture around the system. So depending upon the application you have or depending upon the problem you want to understand, one can choose different type of techniques and Positron and PAC provide such avenues for you. So I will stop here. Thank you very much.