

# MY EXPERIENCE OF WORKING WITH NANO-PARTICLES AT THE ION-ACCELERATOR LABORATORY OF IGCAR

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ABSTRACT. I have been working at the Ion-accelerator ( a 1.7 MeV Tandetron accelerator ) from 1<sup>st</sup>May to 25<sup>th</sup>May 2007. During this time I was studying and working under the esteemed guidance of Mr.Santham Raman and Dr.K.G.M Nair. My theoretical studies have been mainly qualitative and in the following document I shall record the basic structure of the theory and its key points that I realized during my studies regarding the making and characterization of nano-particles. Unfortunately the ion-accelerator was out of order during the period of my stay and hence I could not get a first hand experience of making nano-particles. So on the experimental side I shall briefly sketch the essential methods to which I got exposed to , of characterizing a nano-particle. There too the description shall be qualitative since partly due to time constraints and partly due to lack of pre-requisites I was unable to probe into the rigorous mathematical details.

## 1. A FIRST LOOK AT NANO-PARTICLES

It comes somewhat as a surprise when we first face the fact that the properties of materials in their bulk form is actually dependent on the number of particles present in the bulk. Today in the wake of nano-science we realize that a *cluster* of 20 gold atoms will have drastically different kinds of properties than a single gold atom and also different from that of a gold nugget that a goldsmith is familiar to. As an example of such novel properties we have the following : colloidal gold embedded in glass renders it a purple colour.

Today we realize that as we go on adding atoms to the cluster considered the properties of that cluster keep fluctuating rapidly initially and then from a cluster size of about 1 nano meter to 100 nano meter it will show some novel properties and then again the properties will become asymptotically equal to its bulk properties. (The numbers here are only indicative ). This is the range of dimensions of systems where nano-science is focused, in-between the initial fluctuations and

the beginning of asymptotic behavior.

It should also be noted that the range of cluster dimensions where the novel properties alluded to will be seen is pretty much dependent on the materials considered.

In early years of studying various forms matter things like *smoke, fog, gel, froth, colloids, emulsions, solutions, coloured glass etc* were studied separately. Today Nano-science provides an unifying framework for studying all these things and we realize that they are nothing but different properties of matter obtained as the following key things are varied ::

- The particles in the cluster.
- The cluster dimension.
- The matrix or the substrate in which the nano-particle is embedded.
- The process by which the nano-system was synthesized.

I would here like to mention that from an implementation point of view there can be two approaches to make a nano-cluster:

- Take a macroscopic object and then split it to nano-particles.
- “Bottoms-up” approach. Take atoms and then set them into clusters.

I would like to mention in the passing that it was Richard Feynman who had advocated the second approach and his visions have stood the test of time. Today’s most implementations take the second approach. In this report I shall be mostly concerned with *metal* nano-clusters. We shall have a brief look at the above factors and classification processes of nano-systems in the subsequent sections.

## 2. A BRIEF HISTORICAL BACKGROUND

**2.1. The early beginnings.** Human race has been putting to use the novel properties of these nano-systems long before it came to realize the deeper science behind them. In 4<sup>th</sup> century B.C a thing called “*Cup of Lycurgus*” used to be made in which the embedded colloids of gold and silver produce a green colour when viewed in reflection and a deep reddish-orange colour when viewed in transmitted light.

In 1549 a German chemist *Rudolph Glauber* described a method of preparing “*gold purple* or *ruby glass* by heating a mixture of silicic acid and gold hydroxide to produce embedded colloidal gold particles. Subsequently around 1676 to 1685 similar work that produced

colouration presence of colloidal gold ( by some sources this work was stimulated by the previous work by Glauber ) was carried out by *Andreas Cassius* , a physician in Hamburg,Germany. In 1679 *Johann Knckel vol Lowenstern* , a Potsdam chemist developed a practical and commercial process of producing “*gold ruby glass*”.Such glass became highly prized-particularly subsequent to the death of Kunckel when his secret process was lost until its rediscovery in the nineteenth century.

In 1857 *Michael Faraday* correctly ascribed the red colour of gold-ruby glasses to the presence of finely dispersed colloids of gold. The first systematic probe into these phenomenon was initiated by the historic paper of *Gustav Mie* in 1908 where he successfully applied Maxwell’s equations to explain the absorption and scattering of light from small particles and to account for the origin of colouration due to presence due to the presence of metallic colloids.Mie’s work marks the beginning of the theoretical study of nano-systems. But there wasn’t any motivation towards actually implementing them.

**2.2. Theoretical studies in the 20<sup>th</sup> century begin with Mie.** In the 20<sup>th</sup> century 2 of the most notable theoretical contributions were by *Fröhlich* who in 1937 introduced the fundamental concept of *discrete electronic energy spectrum* when metallic particles become very small and on this basis he calculated the specific heat of small metal particles at low temperatures. Eventually *Kubo and Kawabata* calculated a number of electronic properties ( including the low temperature specific heat) of small metal particles in which the energy levels are quantized due to the finite particle size.The increasing effect of the *surface energy* in determining the physical properties .while going down to the nano-systems was first brought to light by *Buffat and Borel*.Eventually *Rappaport* probed these effects using *Electro Paramagnetic Resonance (EPR) spectroscopy* and *electron diffraction* to investigate the increasing contraction of the crystal lattice of cubic  $SrCl_2$  with decreasing particles size.

**2.3. Feynman gives birth to Nano-technology.** The paramount importance of the historic paper of Mie in provoking theoretical studied of systems at nano-scales cant be over emphasized.Similarly the start of the implementation aspect of nano-science owes itself completely to the historic lecture delivered by *Richard Feynman* on 29<sup>th</sup> December 1959 at *California Institute of Technology (Caltech)* titled “*There’s plenty of room at the bottom*”. What Feynman envisioned in this path-breaking seminar eventually came to be known as *Nano-technology*.

### 3. BASICS OF ION-IMPLANTATION TECHNIQUE TO CREATE NANO-CLUSTERS

One of the most important ways of creating a nano-cluster is by impinging a beam of energetic ions ( of the element with which we want to make the nano-cluster ) on the *substrate* ( also called the *matrix* ). What happens then is also called “*sputtering*”. The impinging ions interact with :

- The sea of valence electrons.
- The lattice sites of the crystal.

If the energy of the impinging ions is low then the interaction is mostly with the electron sea and if it is high then the major interaction is with the lattice. Given the energy ranges that are used in the *Ion-beam accelerator* the impinging atoms “sputter” away the lattice ions and hence get embedded within the matrix. Substrate is so chosen such that the impinging ions are insoluble in it and hence they cluster together inside the matrix as separate globules and what get called as the “clusters”. Generally the clusters are assumed to be spherical and their diameters are reported. It is seen that nano-particles made by the technique of ion-implantation tend to be poly disperse.

We must keep in mind that one of the ultimate aims of nano-technology is to create mono-disperse nano-clusters. They have great potential to cause technological revolutions. One of the promising techniques for that is what is called as *lithography*. But on the flip side nano-clusters created by lithography are not portable whereas the ones created by ion-implantation technique are portable since they get formed as embedded in a solid matrix.

Here we must note the following important aspects of the process::

- The ion-beam is rarely ever homogeneous. So the depth to which the ions would have penetrated the matrix has a statistical spread. This spread is an object of study to determine the quality of nano-particles formed ( here quality is in terms of the size of the particles and the dispersion in the size ). In the lab where I was working the penetration caused by silver ions into the *soda-glass* ( *commercial glass* ) when accelerated to energies like 1 million volts was about 10nm.
- In a particular laboratory generally the energy of the impinging ions is kept fairly constant. Hence what is reported along with

a nano-cluster is the “*dose*” of the ion-beam. “Dose” measures the number of ions impinging the target matrix per unit area. The samples that I worked with were of two types . One had been created with a dose of  $10^{16} Ag^+$  ions per  $cm^2$  and the other was  $3 \times 10^{16} Ag^+$  ions per  $cm^2$ . We must remember that this is the rate at which the ions from the accelerator were hitting the matrix on the surface. The surface density of the ions embedded inside the substrate at various depths will be pretty different. There are various theoretical models that try to predict this variation.

#### 4. CLASSIFICATION OF NANO-CLUSTERS

**From now on whenever we speak of nano-clusters we shall have implicitly made the assumption that the constituent particles are ions of what in bulk form are metal and that the sea of electrons surrounding the nano-cluster ( in which the positive lattice is assumed to be submerged ) can be described *collectively* as a *Plasma* with an electron density labeled as  $N_e$**

4.1. **A general scheme.** To my knowledge there isn’t any internationally standardized way of classifying nano-clusters but then there is a need to do so from the point of view of studying them theoretically. The classification becomes an issue when one has to decide while theoretically modeling a nano-system as to whether to take into account the *quantum* effects that start getting prominent as we decrease the size. The issue is to determine that threshold size till which we can safely use classical electrodynamics to describe a nano-cluster.

We note the following parameters that are used to report the dimension and the compactification of the nano-clusters::

- The cluster diameter labeled as  $2R$  is reported as a gross indicator of the cluster sizes.
- The number of particles per cluster is also reported. Its labeled by  $N$ .
- To indicate the amount of compactification achieved one also reports the ratio of number of particles on the surface of the cluster to the number of particles in the bulk. The ratio is denoted as  $\frac{N_s}{N_b}$ .

Based on these parameters we classify the nano-clusters in the following 3 categories which I am listing along with their parameter ranges::

- **Very Small Clusters**
  - $2 < N \leq 20$
  - $2R \leq 1.1nm$
  - Surface and the inner volume are not distinguishable.
- **Small Clusters**
  - $20 \leq N \leq 500$
  - $1.1nm \leq 2R \leq 3.3nm$
  - $0.5 \leq \frac{N_s}{N_b} \leq 0.9$
- **Large Clusters**
  - $500 \leq N \leq 10^7$
  - $3.3nm \leq 2R \leq 100nm$
  - $0.5 \leq \frac{N_s}{N_b}$

**4.2. Optical properties.** For studying *optical properties* of nano-clusters we generally need to take a slightly different way ( a little more cruder than the above ) way of classifying.

For optical properties what is more important than the absolute size of the nano-cluster is how its size compares to the wavelength of the *incident electromagnetic-wave* which will provoke optical response from it and hence probe the optical properties of the cluster. Here we need to determine whether the theoretical modeling of this cluster-electromagnetic-wave interaction will require the full strength of *Quantum Electrodynamics* or is *Classical Electrodynamics* good enough.

For the above reasons in the context of *Optical Spectroscopy* of metal clusters we look at the ratio  $\frac{R}{\lambda}$  where  $R$  is as explained in the above section and  $\lambda$  is the wavelength of the incident wave. We define nano-clusters with  $\frac{R}{\lambda} \leq 0.01$  to be in the **Quasi-Static Regime**.

We note the following important features of the *Quasi-Static Regime*::

- In this regime the retardation effects of the electro-magnetic field over the cluster diameter is negligible.
- In this size range the multipolar excitation of Mie's theory is overwhelmingly predominated by the dipolar mode.
- For the general range of probes used in the laboratory the Quasi-Static Regime corresponds to the radius of the nano-cluster being in the range  $R < 5nm$

4.3. **Extrinsic and the Intrinsic effects.** Lastly I record the crudest way of classifying nano-particles. We note that the optical properties of the nano-particle are dependent on the dielectric interaction between the nano-particle and its substrate which in turn is dependent on the *relative permittivity* of the nano-cluster. So in the following scheme the focus is whether or not the optical properties i.e the relative-permittivity is a function of the radius of the cluster or it has reached its asymptotic bulk values. Similarly we also want to look at whether the electrodynamic theory of Mie can be considered to be independent of the radius of the cluster or not.

In this context we divide the effect of the size of the nano particle into the following to categories::

- **Intrinsic** if the effect of the size of the nano-particle is manifesting itself as a *quantum theoretic* effect as perceivable effect of boundary condition on the wave-function of the electrons of the metal cluster ,like electron excitation leading to band-gap transition.

We should note that when the size of the cluster is not small enough for quantum effects to be perceivable but the dielectric properties have developed a significant dependence on the radius of the cluster , even then the effects are called *intrinsic*.

- **Extrinsic** if the effect is due to the size manifesting itself as boundary conditions on the mechanical oscillations of the electron sea under electrodynamic perturbation. ( also called *Mie resonances* or *Plasmons* or *Plasmon Polaritons*. ( These terms will be made more precise in the next section)

So we reach at the following crude classification based on the terminology developed in this section::

- $R \leq 10nm$ 
  - Mie's electrodynamic theory shows strong dependence on the cluster radius.
  - Relative permittivity shows strong dependence on the radius of the cluster.
  - The size effects are intrinsic.
- $R \geq 10nm$ 
  - Mie's electrodynamic theory has become independent of the cluster radius.
  - Relative permittivity is almost equal to the bulk values.
  - The size effects are extrinsic.

## 5. A BRIEF LOOK AT THE *Band-Gap*

In the previous section I had introduced the concept of an effect on the nano-particle induced by an electromagnetic wave being *Intrinsic* or *Extrinsic*. I would like to make a few more comments about the *Intrinsic* effects.

The quantum effects that we are alluding to as a part of the intrinsic effects are also sometimes referred to as *Quantum Confinement*. The sea of electrons that surrounds the nano-cluster behave almost like a particle in a finite potential well.

So the quantum effect that we are interested in is the fact that the electronic energies show their discretization very prominently as we decrease the size of the clusters. As the cluster size increases the energy levels become far larger than the gaps between them and we say that the *metal like* behaviors starts to emerge with the formation of *conduction bands* in the metal as the term is understood more commonly in the context of semi-conductors.

Conduction shell or valence shell for an atom by definition is the the electron shell just after the last filled shell. But here when we are concerned with the emergence of metal like properties we are interested in how the conduction shells of the different particles in the cluster interact and group themselves into bands. Conduction band is quasi-continuous over the range in which it is formed and there is distinct energy gap between the bands.

**So conduction bands exist even in very small clusters but only after the size threshold of  $1nm$  they show their typical quasi-continuous behavior within an energy range and a distinct energy gap between 2 bands.**

## 6. CLASSIFYING THE RESPONSE OF THE NANO-CLUSTERS TO ELECTROMAGNETIC PERTURBATION

In the light of the above discussion on band-gap ,when an electromagnetic radiation is incident on a nano-cluster the electron sea responds to it by 2 distinct mechanisms::

- The setting up of **collective electronic oscillations** of the electron plasma which are the *Plasmons* or the *Plasmon Polaritons*. These are mechanical disturbances caused by electrical force of the impinging wave on the electrons.
- The quantum discretization of the electronic energies become prominent at very small sizes. Hence the impinging radiation causes the electrons to undergo **Inter-band transitions** across the band gap.

**Both the above responses emit radiations as an outcome and by detecting and characterizing them like finding out the *resonance* frequencies , Full Width at Half Maximum (FWHM) etc we can get information about the nano-clusters like their average diameters**

## 7. A BRIEF LOOK AT *Plasmons*

We here restate the fundamental picture that we have of the structure of a nano-cluster i.e the constituent particles are metals and that the sea of electrons surrounding the nano-cluster ( in which the positive lattice is assumed to be submerged ) can be described *collectively* as a *Plasma* with an electron density labeled as  $N_e$

Crudely **Plasmon** or **Plasmon Polariton** is a collective excitation of the dense electron gas in the metal.

To stress the fact that Plasmons are mechanical phenomenon driven by electrical forces we can say a little more precisely that Plasmons are **longitudinal collective ( coherent ) oscillations of the electron plasma relative to the crystal lattice**.It essentially brings about a displacement of the *center of mass* of all the electrons in the cluster relative to the positively charged background of the ionic cluster.

I would like to emphasize the fact that one of the most essential features of Plasmon is that it is a **coherent** motion of all the electrons ( i.e they are all oscillating in phase ) brought about by the oscillating electric field acting as an external perturbing force. So the particles satisfy the usual second order differential equation of damped driven oscillator. The forcing term being the electromagnetic wave impinging on the electron and the attraction of the positive lattice being the *drag* term.

**7.1. Classifying Plasmons.** We now realize that within the restrictions imposed by the above conditions there are still 3 distinct types of collective motion possible as listed below. The last among the 3 is what is the most important contributing factor , what is called the **Particle Plasmon or Mie Plasmon**.The three possible types are::

- **Bulk Plasmon**
- **Surface Plasmon**
- **Particle (Mie) Plasmon**

We hereby briefly discuss the essential feature of the above three modes of motion::

- **Bulk Plasmon** is a *collective excitation* of the electron gas in the bulk of the metal which **propagates** as a **longitudinal charge density fluctuation** at a resonance frequency of  $\omega_{pl} = \sqrt{\frac{N_e e^2}{\epsilon_0 m}}$ . This expression can be got from the standard Drude's model of a metal. Very imprecisely we can say that each *quanta* of Bulk Plasmon carries an energy of approximately  $10 - 15eV$ .(Technically the above statement doesn't have much sense)

Since this mode of motion involves *longitudinal* oscillation , this can't be excited by electromagnetic radiation.

- **Surface Plasmon** is the collective motion of electrons orthogonal to the plane of the bounding surface of the cluster. Its clear that the mobility of electrons in a plane parallel to the surface is high( quasi-free approximation) than perpendicular to it because of the retarding attraction of the positive lattice. Let  $\omega_{sp}$  be the frequency of the surface plasmon. We quote here without proof the following relationship  $\omega_{sp} = \frac{\omega_{pl}}{\sqrt{2}}$ .

- **Particle (Mie) Plasmons** are also **longitudinal charge density fluctuations** like the Bulk Plasmon but most importantly they *do not propagate*. Hence they are distinguished from the above types by the often used term **collective electronic oscillations**.

**7.2. The objectives of the Mie Scattering Theory.** What Gustav Mie published in his historic paper of 1908 was an analysis of the above mentioned third kind of Plasmons. That theory has undergone a lot of refinements over the last centuries and computer programs have been written for use in the laboratory. That theory in its modern form is called the **Mie Scattering Theory**.

Mie scattering theory discusses the effect of the following factors on the Mie Plasmons::

- Particle size.
- The effect of the host-matrix interaction on the absorption spectrum.

Effectively this theory takes into account the 2 mechanisms of nano-particle's response to electromagnetic perturbation by making the contribution to the dielectric function  $\epsilon(\omega)$  to come from 2 different sources that is ::

- a *Drude* term from the *collective electronic oscillations*, labeled as  $\epsilon_{intra}(\omega)$ .
- a term representing the contribution of the *inter-band transitions* as described earlier , labeled as  $\epsilon_{inter}(\omega)$ .

## 8. CHARACTERISTICS OF MIE PLASMONS AND THE ASSOCIATED EXPERIMENTAL ASPECTS

I here list the essential features that characterize Mie Plasmons make it different from the other two modes of motion mentioned in the last section and the associated implications of them on experimental techniques::

- **Multipole Response:** Mie Plasmons can be excited by light and most importantly are detectable by pronounced **optical resonance** in the visible or the U.V parts of the spectrum. It must be noted that the Mie Plasmon phenomenon involves the nano-cluster to show *multipole* responses. But if we experimenting in the **Quasi-Static Regime** then we assume that the response is predominantly *dipolar* and we neglect the quadrupole and higher effects while using the theory to analyze experiment.

- **Search For The Resonance points:** Whether we are analyzing the Plasmons as a dipole or a quadrupole or higher the response still has two modes called as the :

- Electric mode
- Magnetic mode

Further in each mode of response the emitted radiation ( what is detected ) can come from 2 distinct process :

- Absorption
- Scattering

Complete theoretical analysis predicts that if we *vary* the incident frequency that is being used to excite the Plasmons then the **complete information about the size of the nano-clusters** is got by analyzing the spectrum in a **neighborhood of the resonance point**.

- **The Resonant Frequency :** of the *Mie Plasmons* depends on the following factors:
  - Dielectric properties of the metal.
  - The surrounding substrate or the matrix.
  - The cluster size and shape.
- **Non-linear optical property:** The phenomenon of *collective charge oscillation* causes a large *resonance enhancement* (denoted as  $f$  ) of the local field at any point within the cluster. This local enhancement is what predominantly dominates the linear and non-linear optical response of the material.

One of the most important commercial applications of nano-clusters is through exploitation of this non-linear optical response. Nano-clusters show a  $3^{rd}$  order of non linearity i.e the polarization vector's components have a term corresponding to sum of all possible ways in which 3 components of the *Electric Field* vector can be chosen and multiplied together. The corresponding coefficient usually denoted as  $\chi^{(3)}$  is **non-zero** for nano-clusters.

We must note that since nano-clusters are generally *Centrosymmetric* the second order term is = 0. Hence  $3^{rd}$  order effect is the lowest order of non-linearity shown by them. This leads the nano-clusters to become a potential source of designable components for opto-electronic devices which make use of the typical effects like the *Kerr effect*.

## 9. CHOICE OF MATERIALS TO DO THE NANO-CLUSTER EXPERIMENTS

**9.1. What is observed ?** The quantity that is analyzed to gauge information about a nano-cluster is the radiation emitted or the absorption coefficient of the sample after it has been perturbed by some electromagnetic wave. More importantly we are interested in the resonant points of the either the absorption spectra or the transmitted spectra.

But as we have noted earlier that the response can come from 2 distinctly different mechanisms of which one is essentially quantum theoretic.

**9.2. Where is the complication ?** So while doing an experiment it is very crucial to be able to resolve the contribution of each of these mechanisms so that analysis can be done properly.

Since the nano-cluster sample getting formed by the process of ion-implantation is generally poly disperse we don't have much control over the size so we don't have much hope of being able to prevent the effect of the size in provoking the quantum effect to predominate. But we have control over the energy of the electromagnetic wave used to probe the sample. Here we exploit the fact that the two responses show **resonance** at different energy scales. Now if the energy required to provoke the 2 mechanisms are well apart then we can choose our probe energy accordingly so that one of the mechanisms can be effectively ignored.

**9.3. Preference for  $Ag^+$  nano-clusters for experiments.** In light of the analysis presented above we have observed that  $Ag^+$  nano-clusters will show a ***strong size dependent optical resonance*** in the **visible spectral range of  $(1.8 - 3)eV$  which is far below the energy required to cause energy required to cause *inter-band transition* whose threshold energy is  $\sim 4eV$ .**

Because of the considerable energy gap between the two phenomenon we can safely assume that the absorption cross-section in the visible region is dominated by the Drude term.

In the experiment that I did I used  $Ag^+$  nano-clusters and while analysis I considered the resonances shown to be coming only due to the Plasmon phenomenon and *not* due to inter-band transitions.

**9.4. Complications if Gold or Copper is used.** Fr Gold and Copper the threshold energy for the resonances due to the 2 processes of response are very close as listed below ::

- Mie Plasmon resonance occurs at  $\sim 2.3eV$ .
- Inter-band transition  $d \rightarrow sp$  transition occurs at  $\sim 2.4eV$ .

Because of the negligible energy gap between the resonant points of the 2 response mechanisms its impossible to resolve as to how much of the contribution is from which process and hence analysis is impossible.

## 10. A BRIEF OUTLINE OF THE 2 EXPERIMENTS THAT I DID

10.1. **The sample characteristics.** The 2 experiments that I did were aimed at characterizing the 2  $Ag^+$  nano-cluster samples that I was given. They had the following characteristics:

- They were created by impinging  $Ag^+$  ions of energy 1 Million eV on ordinary glass strips. The glass piece was a square of about 1.5cm side length.
- The  $Ag^+$  beam was *rastor* scanned on a circular patch of the glass whose radius was 10mm.
- One of the samples was created with a dose of  $3 \times 10^{16}$   $Ag^+$  ions per  $cm^2$  and the other was created with a dose of  $10^{16}$   $Ag^+$  ions per  $cm^2$

10.2. **The experimental techniques and the instruments.** I used two independent methods to determine the size of the nano-particles :

- **Surface Plasmon Resonance (SPR) detection** In this method electromagnetic radiation in the wavelength range of 300nm – 800nm was made to fall on the sample in steps of 0.5nm and an automated analysis system recorded the absorption coefficient for each wavelength. The expectation is that at a certain wavelength of incident radiation there will occur a resonance with the natural frequency of the surface plasmons and the size of the nano-cluster that caused that resonance peak can be estimated from the behavior of the **Absorption coefficient vs Incident circular frequency** graph near the resonance point.

The machine used to do this experiment has been manufactured by the company **Shimadzo** and had the code **UV-3101PC** and was called **UV-VIS-NIR SCANNING SPECTROPHOTOMETER**.

- **Low Frequency Raman Spectrometry (LFRS)** I would first like to emphasize that LFRS technique to determine the size of nano-clusters is **not** due to any of the Plasmon resonance effects that we have been discussing till now. In this process the interaction is between the impingent electromagnetic radiation and the mechanical vibrations of the nano-cluster as a *whole*. For the theoretical analysis we generally consider the clusters to be spherical and decompose the vibrations into *spherical* or *torsional*. What then results as a result of this interaction can be explained by *Raman theory of scattering*. In this experiment it is expected that for *every* size of nano-cluster present a resonant peak shall be observed and an analysis of the graph of **Intensity coefficient of back scattered light vs Raman shift**

near the resonant points will yield information about the size of the nano-cluster that caused that peak.

We must however keep in mind that in LFRS the Plasmon resonance is prevented from showing up by choosing the wavelength of the impinging LASER near the expected resonance wavelength of the total cluster oscillations. We chose the LASER to be tuned to  $488nm$  so that Plasmon resonance doesn't get excited.

The machine used to do this instrument was **Spex double monochromator, Model No. 14018** operating at a wavelength of  $488nm$  (obtained from an adjoining LASER source). The system was set up in a **back scattering geometry**

**10.3. Analysis of the data obtained by the SPR detection technique.** The Spectrophotometer gives the output as a table of the **Absorption coefficient vs Incident wavelength**. I converted it to a data set of **Absorption frequency vs circular frequency** which is given by  $2\pi\nu$  where  $\nu$  is the frequency of the incident wave. Then I plotted two graphs of **Absorption coefficient vs Incident circular frequency** for the 2 samples. Then we used *Origin*(6.1) software to fit the a neighborhood of the resonance points to a *Lorentzian* graph. The neighborhood is so chosen such that the points where the absorption coefficient is *half* the peak value, is also included.

Then I used *Origin* to find the FWHM (Full Width At Half Maximum) i.e the difference of the coordinates on the  $x - axis$  around a local maximum for the two points where the value on the  $y - axis$  is *half* the peak value.

Then I used the standard expression to calculate the *Radius* of the nano-particles which I state below. The symbols are ::

- $r_{metal}$  = radius of the metal nano-cluster.
- $v_f$  = Fermi velocity of the  $Ag^+$  ions.
- $\Delta\omega_{\frac{1}{2}}$  = FWHM on the absorption coefficient vs circular frequency graph.

The expression used is ::

$$r_{metal} = \frac{v_f}{\Delta\omega_{\frac{1}{2}}}$$

10.4. **Analysis of the data obtained by LFRS.** In this experiment the raw data that is obtained is a graph of *Coefficient of intensity for the scattered beam vs The shift in the wave number of the scattered photon from the incident photon*. The graph is plotted by initializing the incident photon's wavenumber (here the incident photon is of 488nm from a LASER source) to 0. Hence the  $x - axis$  is sometimes said to represent the *Raman Shift*.

So the graph effectively plots the intensity coefficient of the scattered photon with respect to wavenumber of the vibration excited in the nano-cluster by this electromagnetic perturbation.

We look at the peak value obtained and then we use the following expression to estimate the *Diameter* of the nano-cluster. The labels in the expression are ::

- $\bar{\nu}$  = The wave-number shift where the peak is observed in the graph.
- $v_t$  = The transverse velocity of sound in  $Ag^+$  ions.
- $d$  = The diameter of the nano-cluster.
- $c$  = The speed of light.

The expression used is ::

$$d = \frac{(0.85)V_t}{\bar{\nu}c}$$

#### 10.5. The Result of the analysis using SPR detection.

- **Sample prepared with a dose of  $10^{16} Ag^+ per cm^2$**

The graph was plotted was *Absorption coefficient vs Incident circular frequency*. Then I used *Origin(6.1)* to fit a *Lorentzian* to each of the peaks and then used *Origin* to read off the FWHM at each of the peaks. The FWHM obtained at each of the peaks were :

- $1.1574 \times 10^{15} sec^{-1}$
- $1.696 \times 10^{15} sec^{-1}$

Each peak corresponds to a specific size group of nano-clusters sensed by this technique. We note that the  $v_f$  for silver is  $1.4 \times 10^{15} nm/sec$ . Therefore by using the expression  $r_{metal} = \frac{v_f}{\Delta\omega_{\frac{1}{2}}}$

we get the following nano-clusters radii:

- $\sim 1.21nm$
- $\sim 0.83nm$

- **Sample prepared with a dose of  $3 \times 10^{16} Ag^+ per cm^2$**

The graph was plotted was *Absorption coefficient vs Incident circular frequency*. Then I used *Origin(6.1)* to fit a *Lorentzian* to each of the peaks and then used *Origin* to read off the FWHM at each of the peaks. The FWHM obtained at each of the peaks were :

- $1.2035 \times 10^{15} sec^{-1}$
- $5.8033 \times 10^{15} sec^{-1}$

Each peak corresponds to a specific size group of nano-clusters sensed by this technique. We note that the  $v_f$  for silver is  $1.4 \times 10^{15} nm/sec$ . Therefore by using the expression  $r_{metal} = \frac{v_f}{\Delta\omega_{\frac{1}{2}}}$

we get the following nano-clusters radii:

- $\sim 1.16 nm$
- $\sim 0.24 nm$

#### 10.6. The result of the analysis using LFRS.

- **Sample prepared with a dose of  $10^{16} Ag^+ per cm^2$**

On the graph of *Coefficient of intensity for the scattered beam vs The shift in the wave number of the scattered photon relative to the incident photon* we identified 3 peaks using the *Peakfit* software and the peaks were identified at the following shifts:

- $15.79 cm^{-1}$
- $30.00 cm^{-1}$
- $37.61 cm^{-1}$

Each peak corresponds to a specific size group of nano-clusters sensed by this technique. We note that the  $v_t$  for silver is  $1660 m/sec$ .

Therefore by using the expression  $d = \frac{(0.85)V_t}{\bar{v}c}$  we find clusters of the following radii getting sensed in the sample::

- $\sim 1.49 nm$
- $\sim 0.78 nm$
- $\sim 0.62 nm$

- **Sample prepared with a dose of  $3 \times 10^{16} Ag^+ per cm^2$**

On the graph of *Coefficient of intensity for the scattered beam vs The shift in the wave number of the scattered photon relative to the incident photon* we identified 4 peaks using the *Peakfit* software and the peaks were identified at the following shifts:

- $11.87 cm^{-1}$
- $21.58 cm^{-1}$
- $29.93 cm^{-1}$
- $34.29 cm^{-1}$

Each peak corresponds to a specific size group of nano-clusters sensed by this technique. We note that the  $v_t$  for silver is  $\sim 1660 m/sec$ . Therefore by using the expression  $d = \frac{(0.85)V_t}{\bar{v}c}$  we find clusters of the following radii getting sensed in the sample::

- $\sim 1.98nm$
- $\sim 1.08nm$
- $\sim 0.78nm$
- $\sim 0.68nm$

## 11. SOME DIRECTIONS FOR RESEARCH

11.1. **The Coherence aspect.** I had emphasized in the very beginning that the *Plasmons* were collective and *coherent* oscillations of the electron plasma. The coherence is an extremely important aspect of the *Plasmons*. After the external electromagnetic perturbations have been switched off the oscillations will stop and this decay process is yet not very clear and we expect that this holds the key to understanding much of the properties of nano-systems. I would like to encode this issue in the form of the following 2 questions ::

- What is the mechanism by which coherence sets in ? What is the time required between the 2 events i.e the electromagnetic radiation reaching the nano-cluster and the plasmons to have started ?
- What mechanisms are responsible for the de-phasing of the oscillations? How rapidly do the collective oscillations lose their phase coherence?

11.2. **The Energy aspect.** After the *de – phasing* has happened the energy has to be dissipated. This *thermalization* process through *internal* and *external* dissipation is still not very well understood. It is conjectured that the energy is lost through the following 3 mechanisms::

- Dissipation in the electron gas.
- Dissipation in the nano-cluster's lattice.
- Dissipation through the (nano-cluster)-(substrate) interactions.

11.3. **The experimental challenge.** In all the experiments that I did the motive was to *characterize* the nano-cluster which has already been formed. The process is *not* targeted to understand the dynamics of nano-systems. But from the frontier application point of view like to study the dynamics of genes or the coiling-recoiling processes of the DNA the important thing is to study the dynamics of systems at nano-meter length scales. Similar is the issue when we want to understand the rise and fall of coherence in Plasmons or the energy dissipation process in nano-clusters.

11.4. **A hope.** Tracking such small systems over such small time scales can be done only through the use of *ultra – shortLASERpulses* of pulse-widths in the order of  $10^{-15}$ secs or femtoseconds or even smaller. Such a LASER can only be obtained by making the frequency profile to have a spread over the *whole* electromagnetic spectrum and yet to have all the frequencies in phase with each other, what is called the **White LASER**.The most promising technology till date for achieving this is CPA (Chirped Pulse Amplification).

I expect that a surge in research towards the making of a **White LASER** will revolutionize the way we try to understand nano-systems and provide deeper insights into the dynamics of biological systems at the genetic level.

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