INDIAN STATISTICAL INSTITUTE

TWENTYSIXTH CONVOCATION ADDRESS

THREE EXCITING AREAS OF EXPERIMENTAL PHYSICAL SCIENCES:
High-temperature superconductors, metal clusters and supermolecules of carbon

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Director, Indian Institute of Science
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6th March 1992

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Mr. President, Mr. Chairman, Professor Bhattacharya, Professor Ghosh, graduating students, ladies and gentlemen.

May I first congratulate the graduating students on this important occasion when they have completed their studies at the Indian Statistical Institute and are starting on a new phase in their profession. I consider the new graduates to be fortunate for having had the opportunity to study in such an institution with high traditions. In these days when excellence is becoming a rare commodity, those of us who are able to be part of institutions of excellence should consider ourselves lucky indeed. I wish the graduating students a very productive and exciting future. The latter seems certain considering the momentous changes occurring in the geopolitical scenario of the world today.

When I was asked by Prof. Ghosh to deliver the 26th Annual Convocation Address, I was slightly hesitant because I do not have the requisite expertise to address statisticians and mathematicians. I, therefore, request you to bear with me and allow me to present some aspects of my research efforts in the last five years. Let me begin this narrative with some personal reminiscences.

Around 33 years ago, I came back to India after my Ph.D. and post-doctoral work in the United States and took up a lecturership at the Indian Institute of Science, Bangalore. I was 25 years old then. I had better offers of positions, but I preferred the lower salary and designation at IISc, since I felt that this Institute offered a better atmosphere for academic research. After joining the Institute, I found that there were no facilities for my research. I had carried out a considerable amount of work before I came to Bangalore in certain areas of spectroscopy and molecular structure and also on some aspects of solid state chemistry. Unfortunately, there was no real spectrometer in the Chemistry laboratories and the one IR spectrometer with the Physics Department was not available to me. My problem was how to do spectroscopic research without a good spectrometer. Similarly, there were no real facilities for solid state chemistry research. I decided to make use of a very ordinary manual ultraviolet-visible spectrophotometer available there to carry out crude low-resolution measurements on organic molecules to derive certain generalisations. I also gathered the available literature on infrared spectra of molecules and succeeded in carrying out a few measurements with the courtesy of friends abroad and in some other laboratories in this country. By making use of such data, I could produce certain correlations. Amazingly, some of the work I did at that time during 1959-61 have become citation classics. At that time, I also wrote two books on chemical aspects of spectroscopy. My work in solid state chemistry began with an old x-ray machine with a very tiny camera which nobody would use today. Slowly, as time went on, I could obtain slightly better facilities, specially when I went to IIT Kanpur. I was a 29-year old Professor when I joined IIT Kanpur. We could build a really great chemistry department there. At no time, however, I had the kind of experimental facilities that I needed. One had to always make up for the deficiency by some sort of innovation. The situation changed somewhat, after I came back to IISc Bangalore around 15 years ago. Although there are good facilities in some of the laboratories in the country, by and large, there is a vast gap between the infrastructure and instrumentation available to us and those available in the advanced countries. Modern research in physical sciences demands much more exacting measurements ; instrumentation today is so fantastic that it becomes difficult to compromise. One still has to innovate by choosing the kind of problem or the area of research that gets recognition even when done here and this is not always easy. It is becoming increasingly difficult to be competitive in experimental research in physical sciences.

I have been fortunate to have pursued certain lines of research that have attracted some attention. This is specially so in the last five years when I have been intensively involved in research in three exciting areas of physical sciences. Let me briefly share with you the agony and ecstasy that I have experienced in carrying out research in these areas.

High-temperature Superconductors

The first area that I will take up pertains to high-temperature superconductivity. High-temperature superconductivity had its beginning when in late 1986, Bednorz and Müller in Switzerland found that a mixture of lanthanum, barium and copper oxides gave rise to superconductivity around 30K. This was a major advance because till then the highest superconducting transition temperature known to man was 23K and for years, there was a stalemate in breaking the 23K barrier. The discovery of 30K superconductivity in an oxide material created great sensation and soon there were efforts everywhere to discover newer materials which would exhibit superconductivity even at higher temperatures.

The discovery of Bednorz and Müller made a great impact on me too. The oxide they had worked on actually belonged to a family which I had studied earlier for some time. I had published a paper on the parent member of this oxide family in the early 1970's from Kanpur. This paper has been quoted by a number of people and continues to be cited, but what is sad is that I could not measure its properties at low temperatures due to the lack of liquid helium facility. I could only measure properties down to liquid nitrogen temperature (77K). With the world-wide rush to discover high temperature superconductors in early 1987, we also got into the act in Bangalore. In March 1987, there was an announcement by Chu & others in the United States that they had discovered an yttrium barium copper oxide which had a superconducting transition close to 90K, well above the liquid nitrogen temperature. These workers had measured the properties of a mixture of yttrium oxide, barium oxide and copper oxide and did not know the identity of the compound. We were also working on the yttrium compound, but were a bit delayed because in solid state chemistry, we do not measure properties of a substance unless we have its complete identity and structure. However, by March 15, 1987 we had a well-characterized compound of yttrium (which was the same as that of Chu) superconducting at 90K. We published this discovery in Nature.

Since 1987, we have been working on a variety of new materials of bismuth, thallium and so on, with higher transition temperatures (up to 130K). We have used chemical ingenuity to modify and improve properties. One of the things we do is to see whether by replacing one metal ion by another based on certain considerations, it is possible to modify or improve certain properties or to create a new series of superconductors. We have been able to discover several new series of superconductors of thallium and bismuth. Let me briefly give an example to illustrate how solid state chemists get motivated to make new materials. There was a class of bismuth-copper oxides which had transition temperatures of 90K or 120K, but all of them showed an unusual structural feature called superlattice modulation. For a while, people thought that the superlattice modulation (which one can easily see in electron diffraction patterns) had something to do with superconductivity. However, soon we could make some bismuth-copper oxides which were not superconducting but had superlattice modulation. There was then the question whether it was possible to have oxides of this family which had no superlattice modulation but were superconducting. We could make such copper oxides in 1990. Obviously, superlattice modulation is unrelated to superconductivity.

Another problem that interested me for some time had to do with the fundamental process related to chemical bonding in cuprate superconductors. We knew that charge transfer from oxygen to copper in these materials was crucial, but had no way of studying this experimentally. Most physicists and theoreticians have considered the charge-transfer energy to be very important but they either ignore it or take it as a constant. I felt that this was not correct. We have, in the last two years, been able to obtain a good experimental measure for the charge-transfer energy by employing photoemission spectroscopy and have shown that charge-transfer energy varies with composition in any given series of superconductors. Clearly, one has to explicitly take charge-transfer energy into account in any model for superconductivity. We are still working on various aspects of superconductors. An aspect of great interest to us in the last one year has been to explore whether we can design a three-dimensional copper-oxide superconductor. This is because all the high-temperature copper oxide superconductors discovered till now have a two-dimensional structure with copper-oxygen sheets. I am happy that we seem to have just succeeded in doing so. If this is true, most models of high-temperature superconductivity in these oxides need to be re-examined, since they all make use of two-dimensionality as an essential feature.

Metal Clusters

An area of vital interest to me in the last one year or so is the area of metal clusters. Let me explain to you what this is. If one takes a piece of metal it shines, it conducts electricity and so on — it has the so-called metallic properties. If one keeps dividing the metal to smaller and smaller bits, eventually one ends up with an atom. Atoms cannot be metallic ; atoms have localised electrons. One can think of a variety of stages between the bulk metal and an atom, involving clusters of atoms of various sizes. Let me recall here that Michael Faraday, whose 200th birth anniversary we recently celebrated, had made colloidal metals of gold and platinum. Colloidal metals have a few thousand atoms in each cluster. However, there can be smaller clusters of 50, 100 or a few hundred atoms. I must mention here that in the area of physical sciences, the study of metal clusters has become an important area in the last two to three years.

It is now known that if one takes certain metals, vapourize them and look at the mass distribution, the atomic clusters which are most stable consist of certain magic numbers of atoms. The fundamental question is : how do the properties of a metal vary when we go from the bulk metal to the atom?

Do the properties vary continuously ? When does the metallicity of a metal disappear as the size of the cluster decreases ? How does the chemical reactivity vary with the size of the metal cluster ? We have been involved in studying these problems and have found them to be fascinating. Experiments in this area are very difficult to perform because of the highly sophisticated instrumentation required where no compromise is possible. We are pursuing this research by employing a variety of techniques including high-energy spectroscopies and atomic resolution microscopy.

Supermolecules of Carbon

The last area of my interest has something to do with the molecular clusters of carbon, an area of intense activity in the last year or so. Scientists have been interested in understanding the nature of carbon molecules in the universe for some time. In an attempt to generate these molecules in the laboratory, Harold Kroto (Sussex), Richard Smalley (Houston) and coworkers studied, in the mid 1980's, the mass spectra of carbon vapours resulting from the ablation of graphite crystals with high energy lasers. To their surprise, they found peaks in the mass spectra due to various carbon species, the most abundant amongst them being a cluster containing 60 carbon atoms. The cluster of sixty carbon atoms has remarkable stability and has a shape similar to a soccer ball involving a framework with an icosahedral hollow cage. Since geodesic domes of a similar shape had earlier been designed by the famous American architect Buckminster Fuller, the C_{60} molecule was named *buckminster-fullerene*. Some people call it *footballene*, but this name has not caught on. Popularly, this molecule has been called *buckyball*.

Along with buckminsterfullerene, C_{60}, the other prominent carbon cluster molecule found in graphite vapours is C_{70}, containing 70 atoms of carbon. The C_{70} molecule has the shape of a rugby ball. This entire family of carbon molecules is referred to as *fullerenes*. One of the large fullerenes one can visualise is C_{540} made up of 540 carbon atoms. Who ever imagined that the element carbon can form molecules which can vapourise ! The fullerenes clearly constitute a new form (or a new allotrope) of carbon different from graphite and diamond that we all know of.

The stability of C_{60} has been attributed to its icosahedral framework. In spite of its stability, it was not possible to study C_{60} in the laboratory until recently, since it was not possible to obtain sufficient quantities of the material. Theoreticians predicted some properties based on various types of calculations, but they could not be verified. The situation however changed towards the end of 1990, when Kratschmer and coworkers found a simple laboratory method to prepare sufficient quantities of C_{60} and C_{70}. Their method involves vapourizing graphite in a conventional bell-jar by passing high current through two graphite electrodes in an atmosphere of helium. The soot collected from the arc was digested with an organic solvent such as toluene. The solid obtained after removing the solvent showed the presence of C_{60} with a minor amount of C_{70}. We have found C_{60} and C_{70} to be present in the soot produced by an ordinary spirit lamp using benzene as the fuel. C_{60} when dissolved in organic liquids gives a magenta coloured solution while the solution of C_{70} is wine red. Note that simple aromatic compounds such as benzene and naphthalene are colourless. It is really unbelievable that we now have supermolecules of carbon which dissolve in solvents and give coloured solutions ! We could not have dreamt of such a possibility, being used to graphite and diamond as the only forms of carbon.

With the availability of a method to produce fullerenes in the laboratory, the topic has become the rage of the day. It has created great excitement in the scientific world comparable to that of high-temperature superconductors in early 1987. The fullerene molecules exhibit most amazing physical and chemical characteristics. In buckminsterfullerene there are two distinct carbon-carbon bond lengths, 1.403Å and 1.434 Å. These distances are in between those in diamond and graphite. While diamond is a perfect insulator, graphite is a conductor. Buckminsterfullerene is an insulator with a band gap of 2.2 eV. The fullerenes love electrons and we can readily add 1, 2, 3 or 4 electrons to C_{60} to give 1−, 2−, 3− and 4− anionic species. C_{60} is a reactive molecule and can undergo several types of reactions. One of the important aspects of interest today is the incorporation of an external atom in the spheroidal cavity. It has to be remembered that C_{60} has a big spherical cavity of 7Å diameter. In Bangalore, we have been able to put an iron atom inside the cage. Excitement in fullerene research is further enhanced by the discovery of superconductivity in alkali doped fullerene compounds. High-pressure studies have shown evidence for metallization of C_{60} under pressure.

A variety of problems related to C_{60} and other fullerenes will occupy the interest of chemists, physicists, materials scientists and others in the next few years. In addition to high-temperature superconductivity, the possibility of making molecular magnets, molecular traps and molecular bearings would be of interest to materials scientists. Use of C_{60} as a veritable store house of organic reagents throws up immense possibilities in synthetic organic chemistry. Use of C_{60} as part of polymeric structures is yet to be explored. Synthesis of higher carbon cluster molecules such as C_{540} is attracting some attention. It is noteworthy that inside the cavity of C_{240}, there would be enough space for placing a C_{60} molecule. Applications aside, the science of fullerenes promises to be exciting for some time to come. Unfortunately, it is extremely difficult to work in this area from India since we do not have the necessary characterization facilities. I do not know how we will ever contribute in a big way to such competitive areas.

Epilogue

I have narrated some aspects of my research which I have found to be exciting in the last few years. I consider myself fortunate that I have had this tremendous opportunity to work on contemporary problems of worldwide interest. Although I have had to struggle hard at every stage due to the lack of some facility or the other, the effort has been worthwhile. I often spend sleepless nights worrying about experiments and facilities, but the effort has given me immense happiness and satisfaction. I do hope that you will not misunderstand me if I say that even in India some excellence in experimental research can be achieved, if one perseveres. I feel that there is no greater joy than doing exciting experimental research. Unfortunately, the experimental culture is slowly disappearing in the country. This causes me great anxiety and concern, but one cannot afford to lose hope.

Once again, may I congratulate the graduating students and thank all of you for your patient hearing.

Thank you.