

**FIFTY-THIRD ANNUAL MEETING OF THE INDIAN ACADEMY OF SCIENCES HELD AT
HYDERABAD—SUMMARIES OF LECTURES DELIVERED**

Physicochemical Properties of Copper Oxides and High-Temperature Superconductivity by P. Ganguly, *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India.*

Several physical properties such as magnetic susceptibility, EPR, optical spectra in visible and in infra-red regions, XPS and XANES studies of several ternary copper oxides having at least one structural feature in common with the structures in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ or $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ are examined. It is concluded from these studies that for networks involving 180° Cu-O-Cu linkages magnetic ordering temperatures may be as high as 1000° K. However, when there are only Cu-O-O-Cu interactions, antiferromagnetic coupling temperature becomes as low as 30–50 K. The latter should be a measure of interplanar exchange strengths or next-nearest neighbour exchange strengths in the superconductors. The importance of three dimensional interactions on Bose condensation temperatures as well as frustrations of antiferromagnetic interactions with respect to T_c is discussed. EPR studies coupled with other studies show the possible existence of charge density waves in compounds derived from La_2CuO_4 , strong copper-oxygen hybridization in square-planar CuO_4 units, existence of high binding energy species in XPS O 1s region arising from such strong covalency which does not seem to affect Cu 2p $3/2$ satellite intensity, correlation between the magnitude of temperature-independent magnetic susceptibility and T_c etc. It is argued that low-dimensionality decreases bandwidth without affecting transfer integral so that in metallization in low dimension is preceded by very strong antiferromagnetic coupling. The formation of peroxidic oxygens and the idea of double valence fluctuation involving Cu^1 and Cu^{3+} and 2O^{2-} and $(\text{O}_2)^{2-}$ is examined. From chemical considerations, the requirements for high T_c superconductors therefore seem to be low-dimensionality brought about by d^9 ions in octahedral symmetry, strong metal-anion hybridization, double valence fluctuation involving anions and cations, high antiferromagnetic coupling strengths etc. Chalcogenides of Ni^{1+} are suggested as likely candidates.

Studies on High Temperature Superconductors at NPL, New Delhi by A. V. Narlikar, *National Physical Laboratory, Hillside Road, New Delhi 110 012, India.*

Studies on high T_c superconductors at NPL are primarily centred around Y-Ba-Cu-O system and the efforts are being directed in the following broad directions: (i) substitution effects on T_c , (ii) to get insight into the mechanism of superconductivity through various characterization techniques like Hall effect studies, Mossbauer spectroscopy, EPR etc., (iii) investigation of both quasi-particle and Josephson tunnelling for both basic and device-oriented research, and (iv) to understand the nature of flux pinning and the factors influencing the critical current density J_c which is the deciding parameter for the large scale utilization of these materials.

Substitution studies carried out at NPL had shown for the first time the possible presence of superconductivity at room temperature ($+26^\circ\text{C}$) when Ba was partly substituted by Sr. Even the so called single phase 123 compound is found to contain an additional phase with T_c of 230 K as revealed by inverse a.c. Josephson effect. These findings have since been corroborated by various research groups in Japan and in USA. The isolation and identification of room temperature superconducting phase is a task of global importance, currently being pursued at NPL. Addition of Zn (presumably going to Cu-site) even in very small concentrations is found to drastically lower T_c . The reason for this is being probed through various characterization tools.

We have used Sn as Mossbauer probe in Y-Ba-Sn-Cu-O system and Mossbauer absorption of Sn has been investigated from room temperature down to 82 K. These studies, which have been carried out in collaboration with Prof. R. P. Sharma and Prof. K. G. Prasad at TIFR have shown that Sn goes partly to Y-site and partly to Ba-site. Sn on Y-site shows no anomaly in the resonance intensity across the transition but there is a significant decrease in the f-factor of the component corresponding to Sn on Ba-site. Through these studies it has been possible to establish that the seat of superconducting instability lies at the linear chains or ribbons of the triple perovskite structure and phonons are involved in superconductivity.

Hall measurements above T_c have shown the current carriers to be holes with carrier density close to 10^{21} per cm^3 . As the temperature is reduced, at the T_c onset there is an anomaly in Hall coefficient analogous to that observed recently by Cohen and his collaborators on La compounds. The anomaly is believed to be due to the granular nature of these materials.

Existence of granular nature provides the basis of inter-grain Josephson tunnelling behaviour manifested by the I-V characteristics of the bulk materials. Zero voltage pair current and quasiparticle tunnelling characteristics are observed at 77 K. In the absence of external magnetic field, self induced steps are also seen. Due to the presence of a large number of randomly oriented weak links the $V-\phi$ curve, instead of showing distinct periods, reveals a large cumulative profile of individual effects of weak links. I-V curves of bulk samples obtained in the presence of impressed microwaves or small d.c. magnetic fields have revealed oscillatory structures, quite similar to those reported recently by Fulton and Dolan on small multiple junctions of Al. These oscillations are believed to result from the tunnelling of individual electrons charging and discharging the junction capacitance. Some preliminary studies have been carried out on both point contacts and break junctions made of 123 compound.

Finally, the observed J_c values on bulk samples, single crystals and thin films of 123 compound have been theoretically analysed to understand the nature flux pinning. The conventional scaling does not work for these materials. The observed data suggest a strong surface pinning and weak bulk pinning. The temperature dependence of the pinning force is indicative of unusual pinning which is most likely to be of proximity type. Excessive rigidity of FLL is yet another factor responsible for low bulk J_c of these materials. Ways to circumvent some of these problems exist.

Studies on the High T_c Oxide Superconductors by G. V. Subba Rao, U. V. Varadaraju, R. Srinivasan* and T. S. Radhakrishnan†, *Materials Science Research Centre, *Department of Physics, Indian Institute of Technology, Madras 600 036, India. Materials Science Laboratory, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India.*

The high T_c ceramic oxide superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_7$ is amenable to chemical substitution and hence fine tuning of some of the superconduct-

ing properties including T_c is possible. Several preliminary studies have been reported on these aspects. Presently, we have synthesized a large number of phases of the type: $\text{LnBa}_2\text{Cu}_3\text{O}_7$ ($\text{Ln} = \text{La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb}$), $\text{Y}_{1-x}\text{Ln}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ ($\text{Ln} = \text{La, Gd, Ho, Tm}$; $x = 0.0 - 1.0$), $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_7$ ($\text{M} = \text{Mn, Fe, Ni, Zn, Pd}$; $0 \leq x \leq 0.25$). A uniform synthesis and oxygen treatment procedure has been adopted to obtain well-defined single phase materials. Our efforts to substitute F (in part) for oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_7$ have not been successful. Superconducting properties of the phases were examined by resistivity (ρ), A.C. susceptibility (χ) and thermoelectric power (α) studies as a function of temperature.

Essential results of the study are: (i) $\text{LnBa}_2\text{Cu}_3\text{O}_7$ exhibit superconductivity with T_c^0 in the range 88–93 K except when $\text{Ln} = \text{La, Pr}$. The superconductivity transitions are sharp (width, $\Delta T_c = 1.5 - 3$ K). (ii) $\text{Y}_{1-x}\text{Ln}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ also exhibit high T_c except when $\text{Ln} = \text{La}$ but Vegard's law is not obeyed. High T_c (>77 K) is encountered in $\text{Y}_{1-x}\text{La}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ up to $x = 0.5$. (iii) The $\alpha - T$ behaviour in pure and Ln-substituted $\text{YBa}_2\text{Cu}_3\text{O}_7$ is nearly linear in the range 300–150 K and shows an anomalous enhancement below 150 K till α drops to zero at T_c . (iv) Our results show that substitution at the Ba-site (by Sr) and at the Cu-site (by transition metal) in $\text{YBa}_2\text{Cu}_3\text{O}_7$ gives rise to a decrease in T_c , in agreement with preliminary results reported by others. Detailed studies are underway.

An Overview of High T_c Superconductivity by E. V. Sampathkumaran, *Solid State Physics group, Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India.*

The identification of a La-Ba-Cu-O system superconducting above ($T_c =$) 30 K by Bednorz and Muller, followed by the attainment of T_c well above 77 K in a Y-Ba-Cu-O system triggered an onslaught of research activity aimed at further enhancement of T_c as well as understanding the origin of such high T_c values. High T_c superconducting oxides known today could be broadly classified into two families — La_2CuO_4 (K_2NiF_4 structure) type compounds and $\text{YBa}_2\text{Cu}_3\text{O}_7$ (defect perovskite). Detailed studies have established that T_c of these compounds is a very sensitive function of oxygen content (and also the position of the oxygen,

vacancy in the latter family of compounds). The experimental results like isotope effect, superconducting gap etc. — relevant to testing the conventional theories seem to be inconclusive. Various questions regarding the dimensionality of superconductivity and the valence state of Cu are also being investigated currently all over the world. Finally, there are often reports claiming the existence of superconductivity at much higher temperatures, but these are of irreproducible nature.

Defects in Liquid Crystals by G. S. Ranganath, *Raman Research Institute, Bangalore 560 080, India.*

Under a polarizing microscope liquid crystals exhibit beautiful, characteristic, optical patterns called textures. They are due to an assembly of topological defects. In each case the texture is determined by the molecular order prevailing in the mesophase, and one can retrieve the structure of the topological defect from the optical data. Such studies have shown that liquid crystals have defect states that are found in such diverse systems as superfluids, magnetic spin systems, crystals, etc. There is an enormous experimental advantage in liquid crystal systems, where with a simple optical technique, one can study topological defects that are otherwise not easily accessible. In addition, liquid crystal systems have on their own thrown up many intellectually challenging problems in the topology of defects. We illustrate some of these features with a nematic liquid crystal as a typical example.

Even in the simplest of the liquid crystals, viz. the nematic phase we find defects with curious and intriguing properties. To-date, chemists have synthesized nematic liquid crystals of cylindrical i.e. uniaxial and orthorhombic (biaxial) symmetries. The uniaxial mesophase is described by a dimensionless non-polar unit vector \mathbf{n} and the biaxial phase by a trihedron of mutually perpendicular dimensionless, non-polar unit vectors \mathbf{a} , \mathbf{b} and \mathbf{c} . We consider here topological defects in these vector fields.

Uniaxial nematics are unique in that they can have both point and line singularities. Detailed analysis shows that only line defects of half-integral strength are singular and that any two such lines can be combined to result in a non-singular structure. Line singularities interact with a force varying inversely as r . Also, in general, they can have angular forces as well, acting between them. Point singularities on the other hand have only integral

strengths. Also we can convert a point defect to its antidefect by taking it once round a line singularity. As a result, in the presence of a line singularity, their combination law is path-dependent, and an even-integral point defect decays into the uniform state. Point singularities interact with a force that is independent of their distance of separation.

By contrast, biaxial nematics have only line singularities. In this case we find half-integral and odd-integral lines to be truly singular, while one can remove completely the singularities associated with even-integral lines. Also three distinctly different classes of half integral lines exist. Any half integral line gets converted into its antidefect in a single circuit around a half-integral line of another class. Thus again, in the presence of a half-integral line, the combination law is not trivial and also an odd-integral line decays into the uniform state. Also any two half-integral lines of different classes get entangled in crossing one another. Though point singularities do not exist one can have Dirac monopoles and Boojas in biaxial nematics. They have structures similar to their counterparts in A phase of ^3He :

In both uniaxial and biaxial nematics we can have nonsingular configurations called solitons. It can be shown that planar, linear and possibly even point solitons exist in these systems. Here also one can draw very close analogies with $^3\text{He-A}$ and magnetic spin systems.

Studying Star Formation Through Infrared by S. N. Tandon, *Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India.*

Life span of a star depends on its mass and for a star more than ten times as massive as Sun it could be as small as ten million years. Thus, during the billions of years of earth's life, several generations of such stars must have been borne in the Galaxy to which our solar system belongs. Young stars of various kinds are often found in groups near the clouds of molecular gas and dust distributed in the Galaxy, and these clouds (which have typical dimensions of several light years and may carry a total mass up to a hundred thousand solar masses) are thought to be sites of star formation. A careful study of such clouds, is needed to answer many questions such as:— what are the main stages through which star-formation proceeds, what are the relative numbers of stars of various masses, do the stars of low and high masses form at similar sites or at distinct

sites, what are the roles of magnetic field, rotation and the perturbations due to young stars?

Due to scattering by the dust, optical depth of a cloud could be as large as hundred attenuation lengths, and the light of a star within is almost completely trapped and converted to heat. Infrared and radio wavelengths provide suitable means of seeing through the clouds. Most of the energy from such clouds emerges in the infrared band (1-1000 μm) and therefore this band plays a special role in studies of star formation. As the atmosphere is almost opaque in the infrared band beyond 30 μm , far-infrared ($> 30 \mu\text{m}$) observations are made with telescopes carried to high altitudes in aircrafts, balloons, etc. The survey carried out by Infrared Astronomy Satellite at 12, 25, 60 and 100 μm wavelengths deserves a mention here. A large number of sites of star-formation in our Galaxy and many galaxies which seem to be going through unusual bursts of star formation activity were detected in this survey.

A one metre size balloon-borne telescope, capable of pointing to a stability of better than one third of a min of arc has been used by TIFR for mapping the emission of several star-forming regions in 120-300 μm wavelength band. These show peaks of emission, due to the dust-gas clumps heated to 20-40° K, which are surrounded by diffuse emission. As an example we consider the observations of Carina Nebula, where about one third of a square degree was mapped by the telescope. In this nebula more than twenty clumps are detected, each having a luminosity more than a thousand times that of Sun. The clumps preferentially occur near the boundaries of the ionized hot gas and may be partly caused by its pressure. The clumps might be carrying in them either young stars or stars in the process of formation. This region, situated about 8,000 light years away, appears to be forming relatively larger proportion of heavy stars in comparison to what is expected from the observations of the stars in the space near Sun. Other clusters of young stars also show a relative deficiency of stars with masses less than a few solar masses, and it is not obvious that this is caused by the observational bias against the faint low mass stars. We can expect the infrared (and other observations) of the future to reveal the sites of formation of low mass stars.

Solar Seismology by H. M. Antia, *Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India.*

Ever since the discovery of solar oscillations in 1960 a considerable effort has been invested to unravel the nature of these intricate velocity fields. These efforts have shown that the observed oscillatory velocity pattern at the solar surface is a result of superposition of some ten million different normal modes of oscillations in the deep solar interior, each with a surface amplitude of the order of 10 cm/s. These oscillations have been observed at the solar surface as Doppler shift of spectral lines. A careful analysis of the frequencies of these seismic disturbances of the Sun, much like those of the Earth, afford the possibility of studying the internal structure and dynamics of the Sun. The study of solar oscillations is therefore referred to as solar seismology. The observed frequencies of normal modes have put severe constraints on theoretical solar models. This has enabled us to estimate the depth of the convection zone and the primordial helium abundance as well as the variation of sound speed and rotation velocity throughout most of the solar interior.

The basic question of how these modes are excited in the Sun remains a matter of controversy. Oscillations in Cepheid variables are known to be self-excited being driven by the κ -mechanism in the ionization zone of these stars. The same mechanism was proposed for the solar oscillations, but later stability calculations seem to indicate that turbulent viscosity in the solar convection zone could stabilize these modes. However, in the absence of a satisfactory theory for turbulent convection, the question of stability of these modes still remains inadequately answered.

An alternative excitation mechanism is that these modes could be driven stochastically by turbulence in the convection zone. The calculated amplitudes of these modes do not appear to agree with observations. However, this cannot rule out the hypothesis of stochastic excitation since these calculations also rely on our current understanding of turbulent fluid motions and are therefore uncertain.

We have carried out extensive study of the stability of solar oscillations including the effect of convection. We find that the stability is essentially controlled by turbulent convection in the outermost layers of the sun. If the effects of convection are ignored in the stability analysis, then almost all the modes turn out to be stable because of the strong

radiative dissipation in the atmosphere, as noted by other workers. Further, most of the stability calculations are based on a local mixing length theory for convection which does not take into account the fact that turbulent convective eddies will penetrate into the atmosphere above the convection zone. Of course, there is no universally accepted prescription to account for this convective overshooting and hence we have tried various reasonable treatments for the coupling between convection and oscillation as well as for the convective overshooting. We find that in all cases where overshooting is included, a large number of solar modes come out to be unstable with the most unstable mode lying in the frequency range of 3–4 MHz. Further the results are not very sensitive to the prescription used to treat convection as long as overshooting is included. For models without overshooting most of the modes do turn out to be stable. Further our results indicate that the modes which have significant growth rates are also observed with significant amplitudes and vice versa.

These results suggest that the issue of stability of solar modes needs to be examined carefully. The main objections against the hypothesis of self-excited solar modes are firstly that no stability calculation finds the fundamental mode to be overstable and this mode is observed although with very low power. Secondly, no nonlinear damping mechanism has yet been proposed which can limit the growth of overstable modes to their observed amplitudes. It is quite conceivable that both the proposed mechanisms complement each other in exciting the solar oscillations.

Two-Dimensional NMR Spectroscopy by Anil Kumar,
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In two-dimensional NMR spectroscopy, the response of a spin-system to two or more impulses, is recorded as a function of two time variables t_1 and t_2 , yielding on double Fourier transformation a spectrum which is a function of two frequency variables. This spectrum is extremely rich in information content and the described algorithm yields the information in an exceedingly efficient manner. As a result, two-dimensional spectroscopy has had revolutionary effect on application of NMR to study of biomolecules.

The information transfer takes place at the

boundary of the time intervals t_1 and t_2 and depending on the action taken on the boundary, various types of two-dimensional spectroscopies are obtained. If the Hamiltonian of the system is switched at the boundary it leads to what is known as resolved 2D spectroscopy; J -resolved 2D spectroscopy, separated local field spectroscopy in solids and NMR imaging. If a coherence transfer is affected at the boundary by application of an impulse then this leads to the broad classes of correlated 2D spectroscopy (COSY). Several modifications of COSY such as spin-echo correlated spectroscopy (SECSY), Relay COSY, Total correlation spectroscopy (TOCSY) and Homonuclear Hartmann Hahn (HOHAHA) have been invented. These are the most important 2D techniques which have led to near complete resonance assignments of the complex NMR spectra of biomolecules. If the information transfer at the boundary is relaxation transfer (achieved by the application of two 90° pulses with a fixed interval τ_m between them — the mixing period) one obtains Nuclear Overhauser Effect Spectroscopy (2D NOE). The 2D NOE experiment has proved to be an extremely powerful technique for resonance assignments in biomolecules and for identifying short proton-proton distances. This has in turn led to obtaining 3-dimensional structures of polypeptides and oligonucleotides in solution. Two-dimensional algorithm is also utilized for indirect detection of forbidden transitions (the so called multiple quantum transitions). Multiple quantum filtered COSY (MQFC) is also a powerful technique for simplifying the complex spectra of biomolecules.

We have recently made several advances in improving the COSY experiment and its applications. Specifically we introduced fixed delays in t_1 and t_2 dimensions with a refocussing 180° pulse in the middle of the delay to improve the cross-peak intensity in COSY and SECSY experiments. A 45° pulsepair filter has been introduced for obtaining pure phase double quantum filtered COSY of three or more coupled spins. This pulse pair filter has been generalized for retaining only certain types of terms in the coherence transfer process. A new method of coherence transfer via longitudinal spin order has been suggested in which the coherence transfer is affected via an intermediate state of longitudinal spin order rather than transverse order. This again leads to pure phase spectrum. A specific scheme has been suggested for two-spin filtering. A unique application of COSY to the spectrum of symmetric molecules oriented in liquid crystal mat-

nces has been carried out. The 2D COSY spectrum is found to contain cross-peaks only between transitions which belong to a given irreducible representation of the symmetry group, thus separating out the transitions belonging to different irreducible representations of the symmetry group.

These developments further enhance the capabilities of the powerful two-dimensional NMR spectroscopy.

Experiments on a Single Layer of Electrons by Ravi Mehrotra, *National Physical Laboratory, Hillside Road, New Delhi 110 012, India.*

A novel system, consisting of a single layer of electrons floating above a liquid helium surface is described. The electron layer can be realized in the laboratory above a helium surface which lies between two horizontal metal plates forming a parallel plate capacitor. A positive voltage is applied to the plate inside liquid helium. This voltage controls the areal density of electrons. The electrons float about 70 Å above the helium surface. At this distance the attractive force towards the surface, due to the image charges of electrons and the repulsive force on the electrons perpendicular to the surface due to the negative electron affinity of liquid helium balance each other. Experiments on this system are generally performed below 1 K.

Such an electron system is an almost ideal 2D system because it is an extremely clean system with no impurities; the substrate (liquid helium) is very smooth being superfluid, the areal density of electrons can be varied over several orders of magnitude, the interaction between the electrons are known exactly, etc. Depending on the density of electrons, the electrons crystallize into a triangular solid below a certain temperature. This is the only Wigner solid known experimentally.

Typical experimental techniques are described in this talk and important experiments carried out so far on this system are mentioned. One important advantage of this system is that the probe with which the electron layer is studied experimentally exists within the system. This probe is provided by the ripplons (quantized capillary gravity waves) existing on the liquid helium surface. The interaction between the electrons and ripplons is known exactly. Future directions in this area are discussed. Research planned at NPL on such a system where the

motion of electrons is restricted in one of the two dimensions in a controlled way is also described. In this way, it should be possible to reduce the dimensionality of this system from two towards one.

Dynamic Experiments with Spin-Glasses by A. K. Raychaudhuri, *Department of Physics, Indian Institute of Science, Bangalore 560 012, India.*

Dynamics of Spins in a spin glass is a topic of current interest. Various probes to study spindynamics with characteristics time scales extending over decades are being used. In this report we present measurements of dynamic susceptibility done on a spin glass and a reentrant spin glass of the system $\text{Fe}_{100-x}\text{Ni}_x\text{Cr}_{20}$.

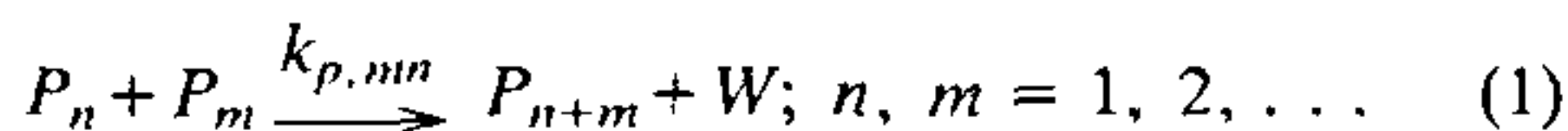
We report here also the measurements dynamic elastic properties of a spin glass ($\text{Fe}_{59}\text{Ni}_{21}\text{Cr}_{20}$) across the transition ($T_g = 16$ K). Unlike previous elastic measurements carried out in the radio frequency range, this is the first measurement of this type on spin glasses in the audio frequency range. A minimum in the sound velocity (V) and a maximum in the internal friction (Q^{-1}) were found at temperatures close to but below T_g . The elastic data were compared with the a.c. susceptibility data taken at similar frequency and were analysed in the framework of theories proposed for sound propagation in spin glass. An estimate of spin correlation time ($\tau = 6.10^{-9}$ sec) at $T = T_g$ had been obtained from elastic measurements. These experiments establish the importance of dynamic elastic measurements on spin-glasses as a new tool to study the dynamics of spin-freezing.

Unequal Reactivity Condensation Polymerizations by S. K. Gupta, *Department of Chemical Engineering, Indian Institute of Technology, Kanpur 208 016, India.*

Bifunctional molecules, for example $\text{HO}-(\text{CH}_2)_n-\text{COOH}$ where the $-\text{OH}$ (A) and $-\text{COOH}$ (B) groups can condense, can be schematically represented as ARB. These molecules, under appropriate conditions, react to give long linear polymer molecules, $\text{A}-\text{R}-(\text{BA})-\text{R}-(\text{BA})-\text{R}-\text{B}$ where $-(\text{BA})-$ represents a polyester linkage

$$\begin{array}{c} \text{O} \\ || \\ \text{---(C---C)---} \end{array}$$

in the above example. Since each of the product molecules has one A group and one B group at the two ends, they can polymerize further, (almost) indefinitely. The reactions taking place can be written schematically as



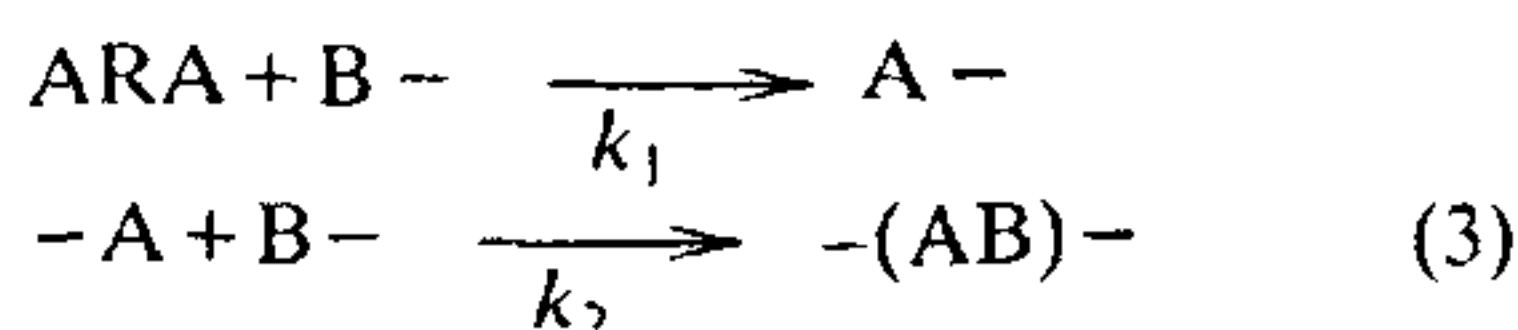
where W is a low molecular weight condensation biproduct, and P_n is a polymer molecule having n repeating monomeric units (called chain length). The rate constant $k_{p, mn}$ has been experimentally found to be independent of m and n in several cases and Flory¹ has used this equal reactivity hypothesis to develop mathematical models for such polymerizations. A similar class of polymerizations involves two bifunctional monomer molecules AR_1A and BR_2B where the functional groups A and B are located on separate molecules. There are several important polymerizations where this Flory's hypothesis is violated, e.g. in the polymerizations of diisocyanates with diols, polyphenylene sulphide, polyether sulphone, uncatalysed polyesters, etc. These can be classified into the following schemes:

(a) *Asymmetric monomers*



where functional groups A_1 and A_2 react with B at different rates characterized by rate constants k_1 and k_2 .

(b) *Induced asymmetry*



where $-$ indicates a polymeric segment. The reactivity of A on ARA changes after any one of them reacts with B.

(c) *Chain length dependent reactivity*

Where the reaction scheme is as in (1), but

$$\begin{array}{l} k_{p, 11} = k_{11} \\ k_{p, mn} = k_p \end{array} \quad (4)$$

Models have been developed for studying the kinetics of such systems. Several interesting conclusions have been reached:—

(i) The molecular weight distribution splits into two, one for odd values of n and one for even values (experimental results on some nonpolymeric catalytic

reactions seem to confirm this).

(ii) The polydispersity index^{1,2} for such polymers produced in isothermal batch reactors is larger than the Flory value of 2.

These models have recently been extended to more complex polymerizations, like those for phenol formaldehyde³ (with phenol having 3 reactive functional groups), and melamine formaldehyde⁴ (with melamine having 6 reactive functional groups). These systems give branched and crosslinked products. These systems also exhibit unequal reactivity of functional groups. For example, in phenol, the para hydrogen reacts at a different rate with the OH of formaldehyde (HOCH_2OH in solution) than the two ortho hydrogens. In addition, the unreacted functional groups in the interior of multiring polymeric chains exhibit lower reactivities than hydrogen on the end rings, possibly due to a shielding phenomena. Theoretical results on such systems show that the branching is maximum when the initial phenol to formaldehyde ratio is about 0.6, an observation that is consistent with industrial practice in the manufacture of resols. Results on melamine formaldehyde are also consistent with some experimental results from the literature.

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2. Gupta, S. K. and Kumar, A., *Reaction engineering of step growth polymerizations*, Plenum, New York, -1987.
3. Pal, P. K., Kumar, A. and Gupta, S. K., *Polymer*, 1981, **22**, 1699.
4. Gupta, S. K., *J. Appl. Polym. Sci.*, 1986, **31**, 2805.

On the use of Size-Extensive and Size-Consistent Models in Quantum Chemistry by D. Mukherjee, Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India.

For a quantum chemical model of viable predictability, it should be size-extensive i.e. it should provide values for extensive quantities (such as energy) that scale properly with the number of particles. It is also highly desirable that the model would be general enough to encompass ground, excited and ionized states and, moreover, should admit of proper dissociation behaviour of molecular systems into the constituent fragments i.e. it should

be size-consistent. Effective hamiltonian formalism furnishes a very natural framework of studying systems of arbitrary complexity and offers a powerful tool for a quantitative modelling of molecular electronic structure. Till very recently, it had been generally accepted that size-extensivity and size-consistency of an effective hamiltonian H_{eff} would be maintained only for a complete valence model space, which is too restrictive a choice and is not generally very practical. We shall argue and show that the size-extensivity of H_{eff} is in no way predicated by this choice. The essential requirements are: (i) the use of a wave-operator Ω that is valid for all the n -valence sectors (valence universality of Ω); (ii) the use of an exponential structure for Ω , [$\Omega \sim \exp(s)$] that ensures asymptotic multiplicative separability; (iii) the use of a normalization that is compatible with (ii); and (iv) if truncations have to be made for a model, then it should be performed on the cluster operator S rather than on Ω . Maintenance of these leads to an open-shell coupled cluster formalism for a general model space. Size-consistency with respect to dissociation into specific channels can then be guaranteed by a careful selection of the model space functions. Several numerical examples will be discussed to illustrate the workability of the formalism, using pair-cluster model ($S \sim S_2$): (a) the interpretation of outer and inner valence ionization potentials where strong correlation effect leads to a breakdown of the orbital picture and to the emergence of satellite structure; (b) prediction of Auger spectrum with satellite features; (c) prediction of excitation energies from closed-shell ground states; (d) generation of potential surfaces where correlation effects lead to avoided crossing, conical intersection or binding behind a Coulombic barrier (as in dicationic species).

Novel Electronic Effects in Radicals and Radical Ions

by Jayaraman Chandrasekhar, *Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India.*

Ab initio and semiempirical molecular orbital methods have been used to make several predictions concerning unusual structural and electronic features associated with radicals and radical ions. A few representative examples follow.

(a) Distonic radical ions, which have their formal charge and radical sites on different atoms are predicted to be more stable than their classical isomers, especially when the electronegativities of

the distal atoms differ substantially. Thus, the silicon based distonic radical cation $\text{H}_2\text{Si}-\text{O}^+\text{H}_2$ is calculated to be preferred over classical SiH_3-OH^+ . The magnitude of this preference in silicon systems is consistently greater than in the corresponding carbon isomers. Stable distonic radical anions are also predicted to exist. The most favourable system for experimental observation would be organoborane radical anions.

(b) The combined stabilizing effect of a donor and an acceptor at a radical is greater than that anticipated from additivity considerations. The additional stabilization, termed the captodative effect, is much larger in radical ions than in neutral radicals. The course of several mass spectral fragmentations is determined by this electronic effect.

(c) In the complexes $\text{Li}(\text{C}_2\text{H}_4)_n$ ($n = 2, 3$), the unpaired electron is delocalized over the π^* orbitals of the ligands. The preferred structures display a Hückel arrangement of interacting π^* orbitals. Möbius topology leads to less stable Jahn-Teller distorted structures.

Theory of Reactions in the Absence of an Activation Barrier by Biman Bagchi, *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India.*

Recent picosecond and subpicosecond laser spectroscopy experiments have revealed several chemically and biologically important reactions in solution, in which the reaction potential surface does not present a barrier to the motion along the reaction coordinate¹. The dynamics of these reactions display diverse and interesting behaviour. They include the dependence of relaxation rate on the solvent viscosity, on the solvent polarity, on temperature and on wavelength of the exciting light. Recent developments in the theoretical description^{2,3} of activationless processes in solution is reviewed and compared with the available experimental results.

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Chemical Synthesis, Spectroscopic and Structural Studies of Short DNA Fragments by K. N. Ganesh, National Chemical Laboratory, Pune 411 008, India.

Protein-Nucleic acid interaction is the single most important recognition system, crucial to most biological processes. Synthetic oligonucleotides can be effectively used to probe protein-nucleic acid interactions by a model system approach. In this lecture, new strategies for large scale (milligram) synthesis of short DNA fragments (6 to 8 mers) are presented. The complete structural analyses of d (CACGTG) using circular dichroism and nuclear magnetic resonance spectroscopy (^1H NMR, COSY, NOESY, ^{31}P NMR) are described. These studies have indicated this hexamer to be present in a distorted B-DNA conformation. The structural effect of sequence studied by 2D ^1H NMR of a related heptamer duplex (GTGGCAC) (CACCGTG) are presented. Since these sequences are related to partial operator region of P22 DNA involved in the binding of Mnt repressor protein, the results have considerable implications to the mechanism of DNA-protein interactions.

In a parallel study, 2D NOESY ^1H NMR Spectral analysis of a 23 Base Pair DNA corresponding to the O_R^3 operator region of λ DNA has been carried out. A new method based on three jump and return pulse sequence was employed to record and assign the labile imino and amino protons of the DNA duplex. The data used for studying chain terminating effects on chemical shifts of imino protons of DNA are presented.

Study of Fast Chemical Reactions by B. Venkataraman, Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India.

Since the probability of encounter of more than three species is infinitely small, it is axiomatic that chemical transformations involving many species must involve elementary steps. Time scale of chemical reactions are known to spread over many orders of magnitude. A new scale, the pT scale, with $pT = -\log_{10} T$ (time in seconds) has been defined and in this scale DNA synthesis has $pT \approx -3$; enzyme synthesis, $pT \approx 3$ to 5; electron transfer reaction $pT \approx 12$.

With the advent of lasers, fast detectors and computers, it has become possible to probe directly into events which take place in time scales of the order of 10^{-13} sec. At such short times, the very

meaning of a chemical reaction becomes very elusive, because of the associated uncertainty in energies being as large as 10% of the bond energy.

In determining the rate of a reaction, we, in reality, determine the statistical average of the rates of several chemical events starting from particular energy states of reactants and ending up in particular energy states of products. In general, these are the vibrational and the rotational states of reactants and products. It is now possible, in elementary reactions, to measure the cross section of a reaction from a particular state (or states) of the reactant(s) to a particular state (or states) of the product(s). In essence, we are now able to probe into the details of a chemical reaction at its most fundamental level.

At the TIFR, we have established over the years, methodologies to measure chemical reaction rates ranging from a few milliseconds to a few picoseconds (10^{-3} to 10^{-12} sec). Temperature jump, which is a chemical relaxation technique, has been employed to study the kinetics of fast transport of protons across membranes in the presence of ionophores¹. Time domain electron spin resonance spectrometry (TDESR) with time resolutions of the order of 200 nanoseconds, has been established to investigate the phenomenon of chemically induced dynamic electron polarization². Solute-solute and solvent-solute interactions³ and the effect of low lying electronic states on spin relaxation times⁴ have been studied with the TDESR spectrometer.

Time correlated single photon counting (TCSPC) techniques have been set up to study fluorescence lifetimes down to 30 picoseconds. The origin of the heterogeneity observed in the fluorescence decay of NADH (Nicotinamide adenosine dinucleotide) has been investigated⁵. The dynamics of diffusion controlled reactions involving charged species has been examined by the study of the fluorescence quenching of cationic dyes, cresylviolet and rhodamine-B by charged quenchers⁶.

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Elucidation of the Exquisite Anti-T Specificity of *Artocarpus integrifolia* Lectin and the Subunit Heterogeneity in Molecule by A. Surolia, *Molecular Biophysics Unit, Indian Institute of Science, Bangalore 560 012, India.*

The Thomsen-Friedenreich (T) antigen is a tumor associated antigen of non-oncofetal origin and is probably one of the few chemically well-defined antigens with a proven link to malignancy; therefore, anti-T probes have enormous potentials in cancer research. Thermodynamic analysis of ligand binding to *Artocarpus* lectin together with their minimum energy conformations has shown that this lectin is highly specific for T-antigen ($\text{Gal}\beta 1 \rightarrow 3\text{GalNAc}$) and fails to recognize conformationally-related disaccharides such as lactose, N-acetylglucosamine and $\text{Gal}\beta 1 \rightarrow 3\text{GlcNAc}$. One of the unusual features of the lectin is that it has strong affinity for both $\text{Me}\alpha\text{Gal}$ and $\text{Me}\alpha\text{GalNAc}$, like the lectins specific for blood group A and B determinants respectively, yet it displays a remarkable specificity for binding to the T-hapten. Further studies were undertaken to resolve this dilemma and define its sugar specificity in considerable detail. Despite its strong affinity for $\text{Me}\alpha\text{GalNAc}$ and $\text{Me}\alpha\text{Gal}$, our studies have revealed that the lectin binds very poorly when galactose and GalNAc are in α -linkage with other sugars in A and B blood group determinants due to unfavourable steric interaction between the lectin and the sugars distal to α -linked Gal or GalNAc. It binds to $\text{Gal}\beta 1 \rightarrow 3\text{GalNAc}\alpha\text{Me}$ with 300 fold affinity over $\text{Gal}\beta 1 \rightarrow 3\text{GalNAc}\beta\text{Me}$ and fails to recognize asialo-GM1 oligosaccharides. Its exquisite specificity for T-antigen together with its virtual non-binding to $\text{Gal}\beta 1 \rightarrow 3\text{GalNAc}\beta\text{Me}$ and asialo-GM1 should make *Artocarpus* lectin a valuable probe for monitoring the expression of T-antigen on the cell-surfaces.

Contrary to an earlier report, our SDS-urea polyacrylamide gels show two distinct bands for the lectin with Mr. 9500 (A subunit) and 10,200 (B subunit) respectively, hence the tetrameric lectin from *Artocarpus* is made of two pairs of non-identical subunits. Our preliminary sequencing studies on the native protein at each cycle gave at least two distinct PTH amino acids. We, therefore, faced considerable difficulty in separating these subunits

for sequence analysis by conventional methods. Isoelectric focussing of the native protein revealed several iso-lectin forms making sequencing task even more daunting. We were, however, able to resolve the peptides in the *Artocarpus* lectin by reverse phase HPLC with 1% TFA-Acetonitrile gradient in 7 distinct fractions to homogeneity. These results further confirm the occurrence of distinct types of subunits in the lectin. We have successfully sequenced more than 25 amino acids from the N-terminus of both types of subunits. Efforts to completely sequence the protein molecule are under progress.

Emerging Concepts in Fluorosis Research by A. K. Susheela, Kamal Sharma and T. K. Das, *Department of Anatomy, All India Institute of Medical Sciences, New Delhi 110 029, India.*

Dental and skeletal fluorosis is a serious health problem in 13 states of India. The main cause of the health problem being ingestion/inhalation of fluoride in excess through water, food, toothpaste, drugs and air (in industrial environment).

In dental fluorosis, the teeth get discoloured, culminate in brown and black teeth with pitting, perforation and get chipped off. Dental fluorosis is known to cause cosmetic and social problems. In skeletal fluorosis, the clinical manifestations begin with pain in the neck, back-bone, hip region, joints and culminate in stiff, immobile and painful joints. Paralysis is common occurrence in late stages and those afflicted have no alternative but to lead a vegetative life.

The pathological changes observed in the bone and dental tissues of fluorosed human patients have been explained at least partly by alterations in the organic matrix of these tissues. These alterations include increased ratio of iduronic acid to glucuronic acid containing sulphated isomers of glycosaminoglycans, reduction in their molecular weight and increased charge density. This, along with reduced cortisol levels leading to abnormal calcium metabolism have been implicated in causing cartilagenous (demineralized) loci formation in bone, mottling and pitting in dental tissues.

Susceptibility to fluorosis is known to vary; it has been found to be determined by pre-existing inflammation, marked by increased serum haptoglobin levels. Those afflicted with skeletal fluorosis have high haptoglobin levels. Those who are residing in endemic areas for fluorosis and ingesting

water with high fluoride content viz. 22.5 ppm (1.5 ppm is the maximum permissible limit) and asymptomatic has very low circulating levels of haptoglobin.

The observations emerging from the studies on sulphated glycosaminoglycans, cortisol and haptoglobin have provided valuable information in understanding the pathogenesis of the disease and the nature of its affliction.

Modelling and control of Automated Manufacturing Systems by N. Viswanadham, *School of Automation, Indian Institute of Science, Bangalore 560 012, India.*

The use of computers in a manufacturing environment has stimulated many new developments and

innovations. Manufacturing technology today stands at the centre stage of what we may call the third industrial revolution and has already strongly influenced the areas of electronics, aerospace and durable goods industries such as garments, wood, etc. The ultimate of these efforts is the creation of the *factory of the future* without people, without paper, working 24 h and 100% inspection.

The lecture presents the architecture of the *factory of the future*, including local area network and material handling system, the modelling issues and finally the computer control systems for real time control of automated factories.

NEWS

METHOD DEVELOPED TO INFLUENCE GENES

Academician Sergei Gershenzon and his colleagues at the Academy of Sciences of the Ukraine, have discovered a regularity important for the selection of agricultural animals and plants.

It is known that physical or chemical impacts can evoke in a live organism a change in genetic information (mutation). This leads to accidental, unpredictable changes in the cell's genetic apparatus which, in most cases, are harmful to the organism. Sergei Gershenzon and his colleagues have developed a method of selective influence on separate genes to obtain the present change in the organism's

properties. It has also been established that as different from all known mutagens, DNA, separated from biological objects (mammals, birds, fish, insects, plants and viruses), and influencing other organisms, evokes in them a strictly definite set of mutations. Research has shown that not only natural DNA but also their synthetic analogues have the same property. (*Soviet Features*, Science and Technology, Information Department, USSR Embassy in India, P.B. No. 241, 25, Barakhamba Road, New Delhi 110 001.)