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Physical chemistry has vastly expanded its boundaries. Modern instrumentation techniques allow for increasingly subtle features of molecular behaviour to be analysed, while computer simulation methods have strongly influenced theoretical analysis. The systems examined by physical chemists have also widened in range and complexity. The topics of interest can vary from the predilections of diatomics placed in selected energy states to structural transitions in lipids and chemical gels. Students and researchers alike desperately need a source which provides a quick update on the remarkable progress being made in a variety of subjects. The series *Annual Reviews of Physical Chemistry* has proved invaluable over the years in this regard.

The format of the series is by now well established. Each volume begins with a Prefatory chapter by an eminent senior physical chemist. In volume 42, E. Hirota presents with characteristic oriental humility his contributions in microwave and infrared spectral studies of reactive intermediates. Accurate determination of potential energy functions for methyl and silyl radicals, extension to photolysis of methyl iodide and the study of species generated in silane discharge plasma are discussed. His account of early difficulties in setting up facilities, partly due to a ban on export of critical diodes by USA, and the years spent without any positive results will strike a sympathetic chord among many experimental physical chemists.

Besides the Prefatory chapter, five other reviews deal with spectroscopy, in one form or the other. K. Muller-Dethlefs and E. W. Schlag describe High-Resolution Zero Kinetic Energy (ZEKE) Photoelectron spectroscopy which they developed in 1984. Conventional photoelectron spectroscopy is a useful technique for determining the electron states and in turn understanding the nature of bonding in molecular systems. Typically, the kinetic energies of the stream of electrons ejected by photoionization are measured in this procedure. Even with the best detectors, the resolution limit seems to be no better than 10 meV. The ZEKE method seeks to overcome this difficulty. If the photon energy exactly matches the energy difference between an ionic molecular state and a neutral state, ionization leads to an electron with zero kinetic energy. By using tunable lasers, resonant two-photon ionization, and an ingenious method to detect ZEKE electrons it is possible to obtain the PE spectrum from state selected molecular systems. Along with the experimental details, several applications to diatomics, polyatomics, hydrogen bonded and van der Waals complexes are provided.

Some recent studies of photolytic generation and ESR investigation of organic radicals and radical ions are reviewed by T. Shida. The examples cited are quite interesting and occasional reinterpretations are provided. However, the article is poorly organized. Although many recent reviews are cited the present review is somewhat unfocused.

Several reviews cover the applications of spectral techniques for studying more complex systems. For example, T. Elsaesser and W. Kaiser have discussed vibrational energy relaxation of polyatomic molecules in the liquid phase as determined by femto- and picosecond spectroscopy. M. D. Ediger has described the use of time resolved optical studies of local polymer dynamics. The nature of information available from such studies is illustrated with examples from anthracene-labelled polystyrene and polyisoprene in dilute and concentrated solutions and in bulk.

C. Dybowski, N. Bansal and T. M. Duncan have highlighted the use of xenon NMR for probing microporous materials. Xenon readily occupies vacant spaces available in polymers, organic lattices and in zeolites. Two of its abundant isotopes have magnetic moments. Most importantly, the NMR chemical shifts of the included xenon is highly sensitive to the local environment and dynamics. Hence xenon NMR offers an excellent opportunity for probing the chemical nature of a variety of materials. There are many problems too, such as excessively large variations in resonance shifts due to non-chemical reasons (collision partner and rate, temperature, etc.) and the weakness and non-specific nature of xenon–host interactions. There is plenty of scope for additional experimental and theoretical studies to make xenon NMR a powerful analytical tool.

The possibility of determining high resolution protein structures in solution using multidimensional NMR has been analysed by T. L. James and V. J. Basus. Although the topic has been thoroughly reviewed on several occasions in view of its significance, a good non-mathematical summary is presented here. The procedures available for accurate spectral assignments are summarized, followed by an account of obtaining distance constraints. Many computational aids are discussed. The performance of NMR is critically evaluated by including comparisons with X-ray diffraction results. Being a particularly active area of research, many recent examples have been cited.

A related review of considerable interest is by A. T. Brünger on the use of simulated annealing in macromolecular crystallography. The difficulties in refining structures of large molecules from X-ray diffraction data are widely known. Simulated annealing has turned out to be a powerful computational technique in solving this problem in many cases. While the methodology has widespread applications in a variety of fields, the author has focused on crystallographic applications. The technical details associated with the procedure are described qualitatively, with many references. A number of representative applications have also been discussed.

Two other reviews discuss the combined use of computational and experimental techniques for analysing complex problems. R. C. Cohen and R. J. Saykally have discussed the methodologies to be used for accurately determining multidimensional potential surfaces and intermolecular dynamics from vibrational–rotational tunneling spectra of small van der Waals complexes. At the other extreme, R. J. D. Miller has considered the problem of vibrational energy relaxation of heme proteins. The corresponding energy exchanges occur in the picosecond range and are distinct from structural dynamics. The progress made and the challenges which remain have been pointed out.

C. Shannon, D. G. Frank and A. T. Hubbard have drawn from their own work to provide a very readable account of electrode reactions of well characterized adsorbed molecules. By combining vacuum techniques and spectral methods to the study of electrochemical processes valuable insights have been obtained on the nature of the electrode interface and its consequence on the chemical processes which occur at the surface.

With a general title 'Reactions on transition metal surfaces', C. M. Friend and X. Xu have discussed transition metal-induced oxygen addition and removal reactions on structurally characterized single crystal metal surfaces. A combination of several ultrahigh vacuum spectral techniques has been used to study the kinetics, product distributions as well as to identify surface intermediates. While the number of systems studied is rather limited, these studies are aimed at a molecular level understanding of surface processes and ultimately of catalysis.

M. Moskovits has also taken a very broad subject for coverage, *viz.* metal clusters. Many intriguing questions are raised, *e.g.* the point at which molecular properties converge to bulk values. However, the author is very selective in the topics discussed. Among the many proposals concerning structure and dynamic of clusters, the jellium model has been evaluated in some detail. There is brief mention of chemistry and spectroscopy of clusters.

Quantum chemical methods have long been the staple of theoretical chemistry. In this volume, the techniques available for studying large systems have been reviewed by R. A. Friesner. A conventional approach is based on the capabilities of the Gaussian 90 program package. The density functional approach for studying large molecules through the DGAUSS program is also discussed. The author has described his own pseudospectral method in some detail and ends with an optimistic outlook. K. Raghavachari has summarized the recent advances made in electron correlation techniques. A brief account of configuration interaction, perturbation methods, coupled cluster techniques and Brueckner orbital methods is provided. The performance of various approaches is critically evaluated with a few representative examples. Both reviews are non-mathematical.

A large number of articles deal with computer simulation studies for a variety of problems. J. L. Barrat and M. L. Klein have discussed recent MD simulations of supercooled liquids near the glass transition. The authors have concentrated on validatating mode coupling theories of the dynamics near the glass transition. Most of the results discussed are for simple model fluids to assess the universal character of glassy behaviour. Dynamics of suspended colloidal spheres is the topic of review by R. B. Jones and P. N. Pusey. After briefly describing the experimental technique of studying Brownian motion of colloidal particles at equilibrium by dynamic light scattering, theoretical descriptions and current status of simulation methods are also discussed. The use of computer simulations for obtaining molecular level understanding of electron transfer reactions in solution and in photosynthetic reaction centres has been described by A. Warshel and W. W. Parson. This review essentially provides an account of the work carried out by the authors in the last few years.

Among other theory-oriented articles is a review by J. E. Martins and D. Adolf on the sol-gel transition. Current kinetic and equilibrium theories are described. Experimental results on kinetics of cluster formation and the nature of cluster structures are evaluated. The remarkable viscoelastic behaviour of incipient gels is also considered. The article is full of subjective comments. In contrasting style, N. S. Lewis has provided a unified discussion on the theory of charge transfer rate constants in semiconductor/liquid interfaces. A basic framework is presented with which charge transfer rates in diverse systems can be understood. Outstanding questions are also clearly stated. A different interfacial system, *viz.* lipid monolayers, is the subject of review by H. M. McConnell. The use of epifluorescence microscopy to study structures and transitions of coexisting lipid monolayer phases at the air–water interface is highlighted. Present theoretical understanding of these systems is described.

Two reviews emphasize the overlap of physical chemistry with materials science. Various aspects of the synthesis of diamond through chemical vapour deposition have been discussed by F. G. Celii and J. E. Butler. After describing the chemical nature of diamond surfaces, various nucleation and surface growth processes are analysed. Several experimental techniques for monitoring the nature of diamond CVD and also theoretical models for the kinetics and growth are summarized. Another highly readable article is on structure and properties of quasicrystals by A. I. Goldman and M. Widom. Diffraction patterns of several alloys with icosahedral symmetry are first described. This is followed by a discussion of structures determined in real space through microscopy, etc. Available theoretical models to account for the occurrence of five-fold symmetry in these structures are presented. Finally, the possibility of quasicrystalline materials possessing unusual electronic and magnetic properties is raised, including a reference to the suggested use of quasicrystals as low-friction coatings on aluminium frying pans.

The final review in the volume, 'Stratospheric ozone depletion' by F. S. Rowland is highly topical. The author was among the first to sound alarm bells on the disastrous consequences of using chlorofluorocarbons on our planet's protective ozone layer. In the present review, he has given a summary of various free radical reactions in the stratosphere with accurate rate constants and their ozone depletion potential. Detailed data from measurements of ozone concentrations at different times and locations are given. Regulations of global CFC emissions enacted in recent years are also listed.

Overall, the volume is overwhelming in its sweep of topics covered. Unfortunately, there is little effort at organization. The grouping of subjects adopted by major journals like the *Journal of Physical Chemistry* (in the contents page) or *Journal of Chemical Physics* (in the subject index) would be useful. Further, there is not much uniformity in the style of presentation. Some authors provide critical reviews, while others are satisfied with a personal account of their contributions. Perhaps the editorial committee worked with impossible deadlines. How else can one explain the poor referencing in some cases, with some 'deleted in proof'? Or the concluding paragraph of an article which reads: 'Future research may illuminate the universality class of gelation, but sociological factors will probably maintain the hugger-mugger; even the most scrupulous researchers may find their expectations anxiously awaiting when they knock upon the laboratory door. Still, science has always progressed despite this limitation, and we expect no less in the field of gelation'. In spite of these criticisms, the volume is strongly recommended for libraries and research groups. There is something of interest for everyone.

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